

State of California  
California Environmental Protection Agency  
AIR RESOURCES BOARD

# **APPENDICES**

## **FOR THE**

Report for the Application and Ambient Air Monitoring  
of Chlorpyrifos (and the **oxon** analogue)  
in Tulare County During Spring/Summer, 1996

Engineering and Laboratory Branch

Monitoring and Laboratory Division

Project No. **C96-041** (Ambient)  
**C96-040** (Application)

Date: April 7, 1998

## APPENDIX I

### SAMPLING PROTOCOL

State of California  
California Environmental Protection Agency  
AIR RESOURCES BOARD

Protocol for the Application and Ambient Air Monitoring  
of Chlorpyrifos (and the oxon analogue)  
in Tulare County During Summer, 1996


Engineering and Laboratory Branch


Monitoring and Laboratory Division

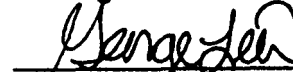
Project No. C96-041 (Ambient)  
C96-040 (Application)

Date: May 22, 1996

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This protocol has been reviewed by the staff of the California Air Resources Board and approved for publication. Approval does not signify that the **contents** necessarily reflect the **views** and policies of the Air Resources Board, nor does mention of trade names or commercial products **constitute** endorsement or recommendation-for use.

Protocol for the Application and Ambient Air Monitoring  
of Chlorpyrifos (and the oxon analogue)  
in Tulare County During Summer, 1996

I. Introduction

At the request (April 28, 1995 Memorandum from John Sanders to Genevieve Shiroma) of the California Department of Pesticide Regulation (DPR), the Air Resources Board (ARB) staff will determine airborne concentrations of the pesticide chlorpyrifos (Lorsban<sup>®</sup>, Dursban<sup>®</sup>) and the oxon analogue for 3-days at an application site and a five week ambient monitoring program in populated areas. This monitoring is done in accordance with Section 140220 of the Food and Agriculture Code which requires the ARB "to document the level of airborne emissions . . . . of pesticides which may be determined to pose a present or potential hazard..." when requested by the DPR. As per the April 19, 1996 memorandum from John Sanders to George Lew, DPR requested that oxon, a degradation product of chlorpyrifos, also be monitored. A literature search for the chemical and toxicological data for the oxon analogue was conducted by the DPR (519196 memo from John Sanders to George Lew) but no information was found. The monitoring will be conducted in Tulare County and is in support of the DPR toxic air contaminant program.

The draft method development results and analysis Standard Operating Procedures submitted by the University of California, Davis (UCD) for chlorpyrifos and the oxon analogue are enclosed as attachment 2.

II. Chemical Properties of Chlorpyrifos

Technical chlorpyrifos [O,O-diethyl O-(3,5,6-trichloro-2-pyridinyl) phosphorothioate] is a crystal, white to amber in color, with a mild mercaptan-like odor. Chlorpyrifos has a molecular weight of 350.59 g/mole and a specific density of 1.398 at 43.5°C. It has a water solubility of 450, 730, and 1,300 µg/L at 10, 20, and 30°C respectively, a Henry's constant of  $4.16 \times 10^{-6}$  atm.m<sup>3</sup>, and a vapor pressure of  $1.7 \times 10^{-5}$  mmHg at 25°C. The half-life ( $t_{1/2}$ ) of chlorpyrifos in several environmental compartments is: 1) Soil  $t_{1/2}$  varies from 12 weeks to 1 day depending on soil type and soil temperature; 2) Surface water (estuarine)  $t_{1/2}$  24 days; and 3) Surface water (fresh, 25°C)  $t_{1/2}$  varies from 120 days (pH 6.1) to 53 days (pH 7.4). Photolytic  $t_{1/2}$  in fresh water at 40°N latitude (depth 10<sup>-3</sup> cm) is reported as 31 days during midsummer and 345 days in midwinter. Increasing the depth to 1 meter increased photolytic  $t_{1/2}$  to 2.7 years.

The acute oral LD<sub>50</sub> of chlorpyrifos for male and female rats is 163 and 135 mg/kg respectively. The LC<sub>50</sub> (96 hour) for rainbow trout is 3µg/L, for bluegill sunfish 2.6 µg/L, and for an estuarine mysid 0.035 µg/L. The OSHA 8-hour time weighted average for personal exposure limit is 0.2 mg/m<sup>3</sup>. Chlorpyrifos has entered the risk assessment process at DPR under the SB 950 (Birth Defect Prevention Act of 1984) based on its mutagenicity and on its relatively low NOEL (No-Observed-Effect-Level).

### III. Sampling

Samples will be collected by passing a measured volume of ambient air through XAD-4 resin. The resin holders are 4-3/4" long x 1-55166" O.D. and made of Teflon. Each holder should contain approximately 30cc of specially prepared XAD-4 resin provided by UCD. The resin will be held in place by stainless steel screens on each side of the resin and between the Teflon support rings. The flow rate will be accurately measured and the sampling system operated continuously with the exact operating interval noted. The resin holders will be covered with aluminum foil during the sampling period. At the end of each sampling period the holders will be capped and placed in a zip-lock plastic bag with an identification label affixed. Any chlorpyrifos present in the sampled ambient air will be captured by the XAD-4 adsorbent. Subsequent to sampling, the sample holder will be transported on dry ice, as soon as reasonably possible to the Department of Environmental Toxicology, University of California, Davis for analysis. The samples will be stored in the freezer (-20 °C) or analyzed immediately.

A sketch of the sampling apparatus is shown in Figure 1. Calibrated rotameters will be used to set and measure sample flow rates. Samplers will be leak checked prior to and after each sampling period with the sampling cartridges installed. Any change in the flow rates will be recorded in the field log book. The field log book will also be used to record start and stop times, sample identifications and any other significant data, including field size, application rate, formulation, method and length of application. Other information which will be collected shall include: 1) the elevation of each sampling station with respect to the field, 2) the orientation of the field with respect to North (identified as either true or magnetic), and 3) an accurate record of the positions of the monitoring equipment with respect to the field, including the distance each monitor is positioned away from the edge of the field and an accurate drawing of the monitoring site showing the precise location of the monitoring equipment and any wind obstacles with respect to the field.

#### A. Application Monitoring

The use pattern for chlorpyrifos suggests that application-site monitoring should be conducted during the months of May, June, or July in Tulare County, and that the application be associated with oranges. Due to the extensive use of chlorpyrifos on oranges during this period, care should be taken so that other applications to nearby groves during the sampling period do not affect sample collection. A three day monitoring period should be established with sampling times as follows; (where the first sample is started at the start of application) application + 1 hour, followed by one 2-hour sample, one 4-hour sample, two 8-hour samples and two 24-hour samples. A minimum of four samplers should be positioned, one on each side of the field. A fifth sampler should be collocated at one position. Ideally samplers should be placed a minimum of 20 meters from the field with a sampling intake approximately 1.5 meters above the ground. Prior to application, background samples will be taken to establish if any chlorpyrifos is detectable. Since chlorpyrifos is extensively used in the area, background samples should collect enough volume (either 12 hours at 15 liters/min., or a shorter period with a higher volume pump) to permit a reasonable minimum detection level. A meteorological station will be set up by DPR to determine wind speed and direction. This station will continue to operate continuously throughout the sampling period collecting data at a minimum of 15 minute

intervals using a data logger. ARB staff will note the degree of cloud cover at the start of application and whenever sample cartridges are changed. Data from the nearest California Irrigation Management Information Systems (CIMIS) station will be provided in the report for temperature and relative humidity. Air samples will be collected with XAD-4 resin using battery powered pumps capable of flows of approximately 15 liters per minute.

The sampling location for the application monitoring has not yet been determined. The site will be chosen with close coordination between ARB staff, the Tulare County Agricultural Commissioner's office and local pesticide applicators.

#### **B. Ambient Monitoring**

The use patterns for chlorpyrifos suggest that ambient monitoring should take place in Tulare County during a 30- to 45-day sampling period in the months of May, June, or July. Three to five sampling sites should be selected in relatively high-population areas or in areas frequented by people. Sampling sites should be in orange growing areas but not immediately adjacent to orange groves. Background samples should be collected in an area distant to chlorpyrifos applications. Replicate (collocated) samples are needed for five dates at each sampling location. The date chosen for replicate samples should be distributed over the entire sampling period. They may, but need not be, the same dates at every site.

Four sampling sites plus an urban background site were selected by ARB personnel from the areas of Tulare County where citrus farming is predominant. Sites were selected for their proximity to the orchards with considerations for both accessibility and security of the sampling equipment. The five sites, as shown on Table 1, were at the following locations: Sunnyside Union Elementary School, Strathmore; Jefferson Elementary School, Lindsay; Kaweah High School, Exeter; UC, Lindcove Field Station, Exeter; ARB Ambient Air Monitoring Station, Visalia (background). Addresses for the sites are listed in Table 1.

<b>TABLE 1. Ambient Sampling Sites</b>	
Sunnyside Union Elementary School 21644 Avenue 196, Strathmore, CA 93267	Gale Gregory, Dist. Superintendent (209) 568-1 741
Jefferson Elementary School 333 Westwood Avenue, Lindsay, CA 93247	Ken Stovall (209) 562-6303
Kaweah High School 21215 Avenue 300, Exeter, CA 93221	Renee Whitson (209) 592-9421
University of California, Lindcove Field Station 22963 Carson Avenue, Exeter, CA 93221	Louis Whitendale, Station Super. (209) 592-2408
Air Resources Board, Ambient Air Monitoring Station 310 N. Church Street., Visalia, CA (Background Site)	Monty Montgomery (209) 228-1 825

Sunnyside Union Elementary School is situated in a sparsely populated area of Strathmore surrounded by agricultural fields, including oranges. The sampling unit will be placed on the roof of one of the classroom buildings which are all single story. There are no buildings or trees near enough to the sampling point to obstruct free air flow.

Jefferson Elementary School is located near the edge of a residential area off Highway 65 in Lindsay. The sampling equipment will be placed on one of the tallest buildings of the school. Trees located near one edge of the building require positioning the sampling equipment near the center of the roof.

Kaweah High School is located north of Highway 198 on Avenue 300. The campus is immediately surrounded by orange groves on all four sides. The sampling equipment will be placed on the north building which is centrally located on the small campus. There were no large structures or trees within prescribed limits to the sampling site.

The fourth sampling site will be located at the University of California, Lindcove Field Station. The site is located, at the edge of the foothills just west of Highway 198. A variety of citrus trees are planted at the field station. Other orange orchards are located throughout the surrounding area. There were no accessible roof tops at this site for the sampling equipment. An open area near the middle of the field station was selected where an existing meteorological station is positioned.

The background monitoring will be conducted at the ARB Monitoring Station in downtown Visalia. The sampling apparatus will be placed on a second story roof near the other ARB monitoring equipment. No orange groves are in existence near the City of Visalia where the background monitoring site was set up.

The samples will be collected by ARB personnel over a five week period from May 28 - June 28, 1996. Twenty-four hour samples will be taken Monday through Friday (4 samples/week) at a flow rate of approximately 15 liters per minute.

#### **IV. Analysis**

A summation of the **S.O.P** is follows: Samples will be extracted with 75 mL of ethyl acetate on a rotating platform shaker for at least 1 hour. One-half (37.5 mL) of the original extract will be measured out using a 50 mL graduated cylinder and transferred quantitatively into a 100 mL round bottom flask. The sample will be evaporated to near dryness, and quantitatively transferred to a hematocrit tube with ethyl acetate (2 mL final volume). All samples will be analyzed directly for chlorpyrifos using a gas chromatography method with a flame photometric detector (FPD), using a 526 nm filter for phosphorus detection. Each set of samples that is worked up will include a control resin blank and three fortified resin blanks. Ambient and application samples that contain residues of chlorpyrifos and/or it's oxon breakdown product will be confirmed either by electrolytic conductivity detector (ELCD) and/or mass selective detector (MSD) operated in selective ion monitoring mode (SIM). The analysis will be conducted under contract by staff at the Trace Analysis Laboratory, Department of Environmental Toxicology, UC Davis. All samples will be stored in an ice chest containing dry ice or a freezer until analysis.

Optional Column Clean Up Procedure: In the advent of interferences a column cleanup procedure and/or a Hall detector will be utilized. (Mourer et al, J. Assoc Off. Anal. Chem Vol 73, 2, 1990). Clean up, when necessary, will be accomplished using a Florisil column. Concentrated extracts will be taken to dryness using a rotary evaporator and brought up in 5 mL of hexane and eluted from a Florisil column with 50 mL of a 5% diethyl ether in hexane solution. Samples will be concentrated using a rotary evaporator and final volume will be adjusted to facilitate analysis.

#### **V. Quality Assurance**

Field quality control (QC) for the application monitoring will include; 1) A field spike (same environmental and experimental conditions as those occurring at the time of sampling) prepared by the ARB Quality Management and Operations Support Branch (QMOSB). The field spike will be obtained by sampling ambient air, collocated with the background sample, through the spiked resin cartridge at 15 L/minute for the same duration as the background sample. 2) Five trip spikes will be prepared by the QMOSB and spiked at five different levels. 3) Replicate samples (collocated) will be collected at one of the four sampling sites. 4) Trip blanks will be obtained at each of the sampling locations.

Field QC for the ambient monitoring will include; 1) Five field spikes (same environmental and experimental conditions as those occurring at the time of ambient sampling) will be prepared by the QMOSB and spiked at five different levels. The field spikes will be obtained by sampling ambient air at the background monitoring site for 24 hour periods at 15 L/minute. 2) Five trip spikes will be prepared by the QMOSB and spiked at five different . levels. 3) Replicate samples will be taken for five dates at each sampling location. 4) Trip blanks will be obtained at each of the five sampling locations. Procedures will follow ARB's 'Quality Assurance Plan for Pesticide Monitoring' (Attachment 1).

The instrument dependent parameters (reproducibility, linearity and minimum detection limit) will be checked prior to analysis. A chain of custody sheet will accompany all samples. Rotameters will be calibrated prior to and after sampling in the field.

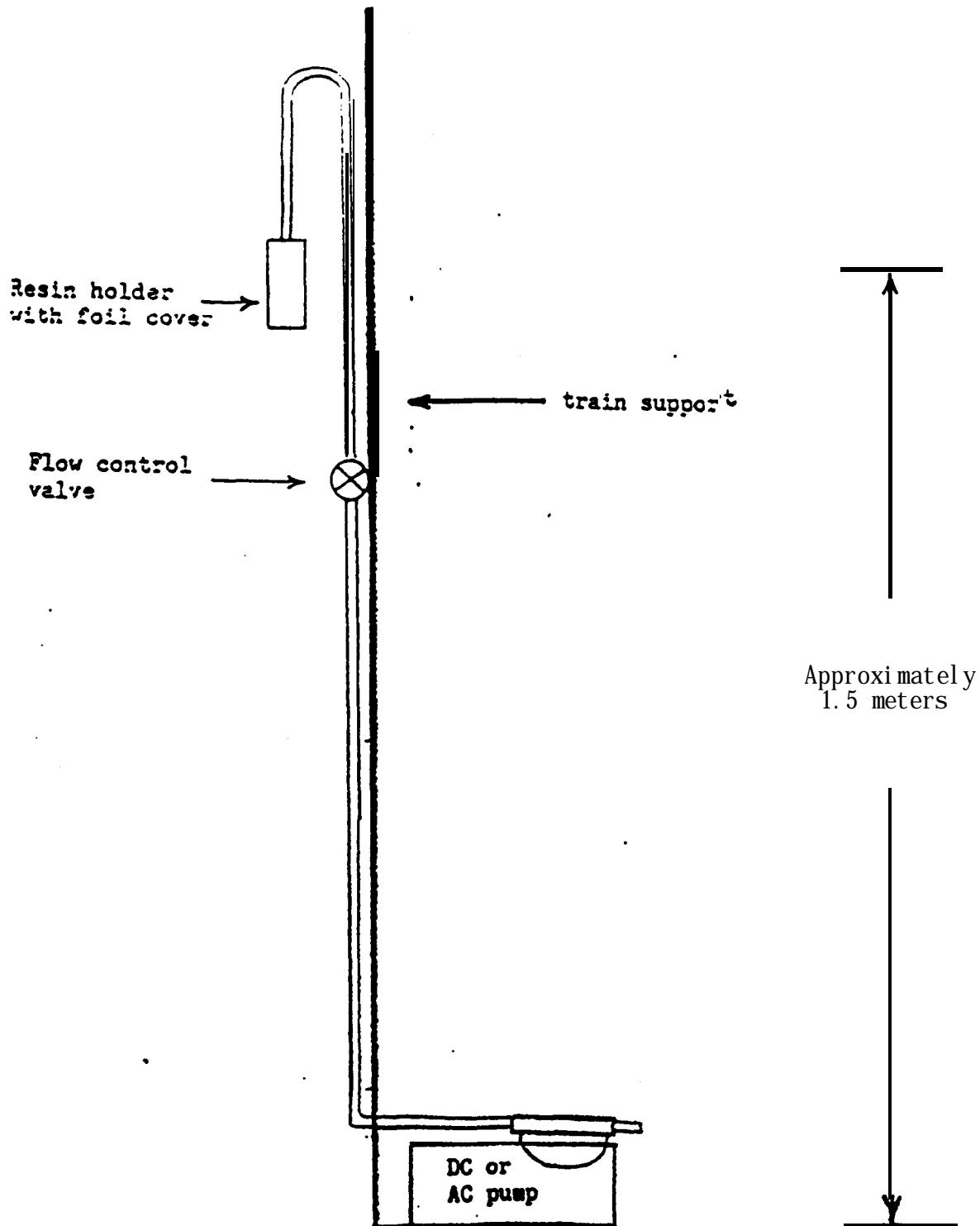
#### **VI. Personnel**

ARB personnel will consist of Kevin Mongar (Project Engineer) and an Instrument Technician.



FIGURE 1

FIELD SAMPLING APPARATUS




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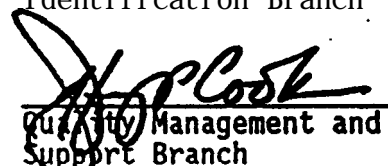
QUALITY ASSURANCE PLAN  
FOR PESTICIDE MONITORING

Prepared by the  
Monitoring and Laboratory Division  
and  
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Revised: February 4, 1994

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**This Quality Assurance Plan has been reviewed by the staff of the California Air Resources Board and approved for publication. Approval does not signify that the contents necessarily reflect the views and policies of the Air Resources Board, nor does mention of trade names or commercial products constitute endorsement or recommendation for use.**

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## QUALITY ASSURANCE PLAN FOR PESTICIDE MONITORING

### I. Introduction

At the request of the Department of Pesticide Regulation (DPR), the Air Resources Board (ARB) documents the "level of airborne emissions" of Specified pesticides. This is usually accomplished through two types of monitoring. The first consists of one month of ambient monitoring in the area of, and during the season of, peak use of the specified pesticide. The second is monitoring near a field during and after (up to 72 hours) an application has occurred. These are referred to as ambient and application monitoring, respectively. To help clarify the differences between these two monitoring programs, ambient and application are highlighted in bold in this document when the information applies specifically to either program. The purpose of this document is to specify quality assurance activities for the sampling and laboratory analysis of the monitored pesticide.

#### A. Quality Assurance **Policy** Statement

**It is** the policy of the ARB **to** provide DPR with as reliable and accurate data as possible. The goal of this document is to identify procedures that ensure the implementation of this policy.

#### B. Quality Assurance Objectives

**Quality** assurance objectives for pesticide monitoring are: (1) to establish the necessary quality control activities relating to site selection, sample collection, sampling protocol, sample analysis, data reduction and validation, and final reports; and (2) to assess data quality in terms of precision, accuracy and completeness.

### II. Siting

Probe siting criteria for ambient pesticide monitoring are listed in TABLE 1. Normally four sites will be chosen. The monitoring objective for these sites is to measure population exposure near the perimeter of towns or in the area of the town where the highest concentrations are expected based on prevailing winds and proximity to applications. One of these sites is **usually** designated to be an urban area "background" site and is located away from any expected applications; however, because application sites are not known prior to the start of monitoring, a "zero level" background may not **occur**. Detectable levels of some pesticides may also be found at an urban area background site if they are marketed for residential as well as **commercial** use.

Probe siting criteria for placement of samplers near a pesticide **application** for collection of samples are the same as ambient monitoring (TABLE 1). In addition, the placement of the application samplers should be **to obtain** upwind and downwind concentrations of **the** pesticide. Since winds are variable and do not always conform to expected patterns, the goal is to surround the

application field with one sampler on each side (assuming the normal rectangular shape) at a distance of about 20 yards from the perimeter of the field. However, conditions at the site will dictate the actual placement of monitoring stations. Once monitoring has begun, the sampling stations will not be moved, even if the wind direction has changed.

### III. Sampling

All sampling will be coordinated through the County Agricultural Commissioner's Office and the local Air Quality Management District (AQMD) or Air Pollution Control District (APCD). Monitoring sites will be arranged through the cooperation of applicators, growers or owners for application monitoring. For selection of ambient sites, ARB staff will work through authorized representatives of private companies or government agencies.

#### A. Background Sampling

A background sample will be taken at all sites prior to an application. It should be a minimum of one hour and longer if scheduling permits. This sample will establish if any of the pesticide being monitored is present prior to the application. It also can indicate if other environmental factors are interfering with the detection of the pesticide of concern during analysis.

While one of the sampling sites for ambient monitoring is referred to as an "urban area background," it is not a background sample in the conventional sense because the intent is not to find a non-detectable level or a "background" level prior to a particular event (or application). This site is chosen to represent a low probability of finding the pesticide and a high probability of public exposure if significant levels of the pesticide are detected at this urban background site.

#### B. Schedule

Samples for ambient pesticide monitoring will be collected over 24-hour periods on a schedule, in general, of 4 samples per week for 4 weeks. Field application monitoring will follow the schedule guidelines outlined in TABLE 2.

#### C. Blanks and Spikes

Field blanks should be included with each batch of samples submitted for analysis. This will usually require one blank for an application monitoring and one blank per week for an ambient monitoring program. Whenever possible, trip spikes should be provided for both ambient and application monitoring. The spiked samples should be stored in the same manner as the samples and returned to the laboratory for analysis.

#### D. Meteorological Station

Data on wind speed and direction will be collected during application monitoring by use of an on-site meteorological station. If appropriate

equipment is available, temperature and humidity data should also be collected and all meteorological data recorded on a data logger. Meteorological data are not collected for ambient monitoring.

#### E. Collocation

for both ambient and application monitoring, precision will be demonstrated by collecting samples from a collocated sampling site. An additional ambient sampler will be collocated with one of the samplers and will be rotated among the sampling sites so that duplicate samples are collected at at least three different sites. The samplers should be located between two and four meters apart if they are high volume samplers in order to preclude airflow interference. This consideration is not necessary for low (<20 liters/min.) flow samplers. The duplicate sampler for application monitoring should be downwind at the sampling site where the highest concentrations are expected. When feasible, duplicate application samples should be collected at every site.

#### F. Calibration

Field flow calibrators (rotometers, flow meters or critical orifices) shall be calibrated against a referenced standard prior to a monitoring period. This referenced standard should be verified, certified or calibrated with respect to a primary standard at least once a year with the method clearly documented. Sampling flow rates should be checked in the field and noted before and after each sampling period. Before flow rates are checked, the sampling system should be leak checked.

#### G. Flow Audit

A flow audit of the field air samplers should be conducted by an independent agency prior to monitoring. If results of this audit indicate actual flow rates differ from the calibrated values by more than 10%, the field calibrators should be rechecked until they meet this objective.

#### H. Log Sheets

Field data sheets will be used to record sampling date and location, initials of individuals conducting sampling, sample number or identification, initial and final time, initial and final flow rate, malfunctions, leak checks, weather conditions (e.g., rain) and any other pertinent data which could influence sample results.

#### I. Preventative Maintenance

To prevent loss of data, spare pumps and other sampling materials should be kept available in the field by the operator. A periodic check of sampling pumps, meteorological instruments, extension cords, etc., should be made by sampling personnel.

TABLE 1. PESTICIDE PROBE SITING CRITERIA SUMMARY

The following probe siting criteria apply to pesticide monitoring and are summarized from the U.S. EPA ambient monitoring criteria (40 CFR 58) which are used by the ARB.

Height Above Ground <u>(Meters)</u>	Minimum Distance From <b>Supporting Structure</b> <u>(Meters)</u>		<u>Other Siting</u> <u>Criteria</u>
	<u>Vertical</u>	<u>Horizontal</u>	
2-15	1	1	<ol style="list-style-type: none"> <li>1. Should be 20 meters from trees.</li> <li>2. Distance from sampler to obstacle, such as buildings, must be at least twice the height the obstacle protrudes above the sampler.</li> <li>3. Must have <b>unrestricted</b> air-flow <del>270</del> around sampler.</li> <li>4. Samplers at a collocated site (duplicate for quality assurance) should be <b>2-4</b> meters apart if samplers are high flow, <b>&gt;20</b> liters per minute.</li> </ol>

TABLE 2. GUIDELINES FOR APPLICATION SAMPLING SCHEDULE

All samplers should be sited approximately 20 yards from the edge of the field; four samplers to surround the field whenever **possible**. At least one site should have a collocated (duplicate) **sampler**.

The approximate sampling schedule for each station is listed below; however, these are only approximate guidelines since starting time and length of application will dictate variances.

- Background sample (minimum 1-hour sample: within 24 hours prior to application).
- Application + 1 hour after application combined sample.
- **2-hour** sample from 1 to 3 hours after the application.
- **4-hour** sample from 3 to 7 hours after the application.
- 8-hour sample from 7 to 15 hours after the application.
- **9-hour** sample from 15 to 24 hours after the application.
- 1st **24-hour** sample starting at the end of the **9-hour** sample.
- 2nd **24-hour** sample starting 24 hours after the end of the **9-hour** sample.



#### IV. Protocol

Prior to conducting any pesticide monitoring, a protocol, using this document as a guideline, will be written by the ARB staff. The protocol describes the overall monitoring program, the purpose of the monitoring and includes the following topics:

1. Identification of the sample site locations, if possible.
2. Description of the sampling train and a schematic showing the component parts and their relationship to one another in the assembled train, including specifics of the sampling media (e.g., resin type and volume, filter composition, pore size and diameter, catalog number, etc.).
3. Specification of sampling periods and flow rates.
4. Description of the analytical method.
5. Tentative test schedule and expected test personnel.

Specific sampling methods and activities will also be described in the monitoring plan (protocol) for review by ARB and DPR. Criteria which apply to all sampling include: (1) chain of custody forms (APPENDIX I), accompanying all samples, (2) light and rain shields protecting samples during monitoring, and (3) storing samples in an ice chest (with dry ice if required for sample stability) or freezer, until delivery to the laboratory. The protocol should include: equipment specifications (when necessary), special sample handling and an outline of sampling procedures. The protocol should specify any procedures unique to a specific pesticide.

#### V. Analysis

Analysis of all field samples must be conducted by a fully competent laboratory. To ensure the capability of the laboratory, an analytical audit and systems audit should be performed by the ARB Quality Management and Operations Support Branch (QMOSB) prior to the first analysis. After a history of competence is demonstrated, an audit prior to each analysis is not necessary. However, during each analysis spiked samples should be provided to the laboratory to demonstrate accuracy.

##### A. Standard Operating Procedures

Analysis methods should be documented in a Standard Operating Procedure (S.O.P.) before monitoring begins. The S.O.P. includes: instrument and operating parameters, sample preparation, calibration procedures and quality assurance procedures. The limit of quantitation must be defined if different than the limit of detection. The method of calculating these values should also be clearly explained in the S.O.P.

1. Instrument and Operating Parameters

A complete description of the instrument and the conditions should be given so that any qualified person could duplicate the analysis.

2. Sample Preparation

Detailed information should be given for sample preparation including equipment and solvents required.

3. Calibration Procedures

The S.O.P. plan will specify calibration procedures including intervals for recalibration, calibration standards, environmental conditions for calibrations and a calibration record keeping system. When possible, National Institute of Standards and Technology traceable standards should be used for calibration of the analytical instruments in accordance with standard analytical procedures which include multiple calibration points that bracket the expected concentrations.

4. Quality Control

Validation testing should provide an assessment of accuracy, precision, interferences, method recovery, analysis of pertinent breakdown products and limits of detection (and quantitation if different from the limit of detection). Method documentation should include confirmation testing with another method when possible, and quality control activities necessary to routinely monitor data quality control such as use of control samples, control charts, use of surrogates to verify individual sample recovery, field blanks, lab blanks and duplicate analysis. All data should be properly recorded in a laboratory notebook.

The method should include the frequency of analysis for quality control samples. Analysis of quality control samples are recommended before each day of laboratory analysis and after every tenth sample. Control samples should be found to be within control limits previously established by the lab performing the analysis. If results are outside the control limits, the method should be reviewed, the instrument recalibrated and the control sample reanalyzed.

All quality control studies should be completed prior to sampling and include recovery data from at least three samples spiked at least two concentrations. Instrument variability should be assessed with three replicate injections of a single sample at each of the spiked concentrations. A stability study should be done with triplicate spiked samples being stored under actual conditions and analyzed at appropriate time intervals. This study should be conducted for a minimum period of time equal to the anticipated storage period. Prior to each sampling study, a conversion/collection efficiency study should be conducted under field conditions (drawing ambient air through spiked sample media at actual flow rates for the recommended sampling time) with three

replicates at two spiked concentrations and a blank. **Breakthrough** studies should also be conducted to determine the capacity of the adsorbent material if high levels of pesticide are expected or if the suitability of the adsorbent is uncertain.

## VI. Final Reports and Data Reduction

The mass of pesticide found in each sample should be used along with the volume of air sampled (from the field data sheet) to calculate the mass per volume for each sample. For **each sampling** date and site, concentrations should **be** reported in a table as **ug/m<sup>3</sup>** (microgram per cubic meter). When the pesticide exists in the vapor phase under ambient conditions, the concentration should also be reported as ppbv (parts per billion, by volume) or the appropriate volume-to-volume units. Collocated samples should be reported separately as raw data, but then averaged and treated **as a** single sample for any data summaries. For samples where the end flow rate is different from that set at the start of the sampling period, the average of these two flow rates should be used to determine the total sample volume; however, the minimum and maximum concentrations possible for that sample should also be presented.

The final report should indicate the dates of sampling as well as the dates of analyses. These data can be compared with the stability studies to determine if degradation of the samples has occurred.

Final reports of all monitoring are sent to the Department of Pesticide Regulation, the Agricultural **Commissioner's** Office, the local **AQMD** as **well** as the applicator and/or the grower. Final reports are available to the public by contacting the ARB Engineering Evaluation Branch.

### A. Ambient Reports

The final report for ambient monitoring should include a map of the monitored area which shows nearby towns or **communities** and their relationship to the monitoring stations, along with a list of the monitoring locations (e.g., name and address of the business or public building). A site description should be completed for any monitoring site which might have characteristics that could affect the monitoring results (e.g., obstructions). For ambient monitoring reports, information on terrain, obstructions and other physical properties which do not conform to the siting criteria or may influence the data should be described.

Ambient data should be summarized for each monitoring location by maximum and second maximum concentration, average (using only those values greater than the minimum quantitation limit), total number of samples **and** number of samples above the minimum quantitation limit. For this **purpose**, **col** located samples are averaged and treated as a single sample.

### B. Application Reports

Similarly, a map or sketch indicating the general location (**nearby towns, highways, etc.**) of the field chosen for application monitoring **should be included** as well as a **detailed** drawing of the field itself and the **relative** positions of the monitors. For application monitoring reports, **as**

much data as possible should be collected about the application conditions (e.g., formulation, application rate, acreage applied, length of application and method of application). This may be **provided** either through a copy of the Notice of Intent, the Pesticide Control Advisor's (PCA) recommendation or completion of the **Application Site Checklist (APPENDIX 11)**. Wind speed and direction data should be reported for the application site during the monitoring period. Any additional meteorological data collected should also be reported.

### C. Quality Assurance

All quality control and quality assurance samples (blanks, spikes, etc.) analyzed by the laboratory must be reported. Results of all method development and/or validation studies (if not contained in the S.O.P.) will also be reported. The results of any quality assurance activities conducted by an agency other than the analytical laboratory should be included in the report as an appendix. This includes analytical audits, system audits and flow rate audits.

# **Standard Operating Procedure for the Analysis of Chlorpyrifos and Chlorpyrifos Oxon in Ambient Air**

## **1. SCOPE**

The method utilized is a gas chromatographic method with a flame photometric detector (FPD) and a 526 nm filter that is selective for phosphorus compounds. This method has been used by Environmental Toxicology personnel for the analysis of organophosphates in air.

## **2. SUMMARY OF METHOD**

Exposed XAD-4<sup>®</sup> resin samples are stored either in an ice chest with dry ice or at -20 °C in a freezer. Samples are extracted with 75 mL ethyl acetate and an aliquot is concentrated prior to injecting 3 µL on to a gas chromatograph equipped with a flame photometric detector.

## **3. INTERFERENCES/LIMITATIONS**

Potential interferences may arise due to contaminants in laboratory solvents, reagents, glassware and/or apparatus. A reagent blank must be run through the method procedure and analyzed with each set of samples.

## **4. EQUIPMENT AND CONDITIONS**

### **Instrumentation**

Hewlett-Packard 5890 Series II gas chromatograph  
Hewlett-Packard 7673 Autosampler  
Perkin-Elmer TurboChrom<sup>®</sup> Data System  
Microsoft Excel\*, version 7.0

Injector : 250 °C

Detector: 250 °C

Column: Rxt-1 30 m x 0.53 mm wide bore capillary with a 1.5 µm film thickness

Temperature program: initial: 180 °C, hold 1 min, ramp to 220 °C @ 10 °C/min; hold 1 min. Retention time : chlorpyrifos oxon = 4.68 min ; chlorpyrifos = 4.87 min.

Flows:

Carrier (He) = 20 mL/min

make up(He) = 10 mL/min

a i r = 115 mL/min

hydrogen = 100 mL/min

## B. Auxiliary Apparatus

1. **Rotary** platform shaker
2. 100 **mL** round bottom flasks
3. 50 **mL** graduated cylinders
4. Rotary evaporator
5. Disposable **pipets**
6. Nitrogen evaporator (**N-Evap7**)
7. Graduated 15 **mL** centrifuge tubes
8. Autosampler vials and screw caps

## C. Reagents

1. Ethyl acetate, pesticide grade
2. **Chlorpyrifos**, Dow Elanco 99% or equivalent
3. **Chlorpyrifos oxon**, Dow Elanco 95% or equivalent

## 5. **ANALYSIS OF SAMPLES**

1. A solvent blank will be **analyzed** with each set of samples. The blank must be **free** of interferences for the analysis of both chlorpyrifos and chlorpyrifos **oxon**.
2. Three resin fortification samples must be fortified, extracted and analyzed with each set of samples.
3. Allow samples to come to room temperature and add 75 **mL** of ethyl acetate. Cap the sample and swirl for one hour on a rotary platform shaker.
4. Quantitatively transfer 37.5 **mL** to a 100 **mL** round bottom flask and evaporate the solvent to near dryness using a rotary evaporator.
5. Transfer sample using small aliquots of ethyl acetate to a graduated centrifuge tube. Adjust sample to an appropriate volume for injection on to the **GC-FPD**.
6. Transfer an aliquot of the adjusted sample to an Autosampler vial.
7. Inject 3 **μL** of sample, along with the appropriate standard concentrations for chlorpyrifos and chlorpyrifos **oxon**, into the gas **chromatograph**. If the peak area for either the parent or the **oxon**, is larger than the highest standard, dilute the sample with ethyl acetate and re-inject.
8. Calculate the mass in **μg** based on the linear regression curve for **TurboChrom** and the appropriate dilution factors.

Concentration(**μg/mL**) x Dilution **Factor** (**mL**)/Sample = **μg/sample**.

## 6. QUALITY ASSURANCE

### A Instrument Reproducibility

Triplicate injections of three standards at five different concentrations were made to establish the reproducibility of the instrument. The data for chlorpyrifos and the **oxon** are given in Table 1 and Table 2 respectively.

Table 1. Instrument Reproducibility for **Chlorpyrifos**

Chlorpyrifos Injected (pg/ul)	Integration Counts	Percent (%)
25	10682 ± 314	± 2.94
50	20852 ± 961	± 4.60
100	41856 ± 1247	± 2.98
200	88037 ± 822	• 0.93
400	166594 ± 9457	± 5.68

Table 2. Instrument Reproducibility for **Chlorpyrifos Oxon**

Chlorpyrifos Oxon Injected (pg/μL)	Integration Counts	Percent (%)
25	8503 ± 826	± 9.71
50	17831 ± 1487	± 8.34
100	35611 ± 4134	± 11.6
200	73796 ± 6627	± 8.98
400	143990 ± 19886	± 13.8

### B. Linearity

A five point calibration curve of chlorpyrifos and chlorpyrifos **oxon**, with concentrations ranging from 0.025  $\mu\text{g/mL}$  to 0.40  $\mu\text{g/mL}$ , was injected 5 times during the course of a run that included a total of 72 injection. The run included **XAD** resin samples and fortified resin samples. The corresponding equations and correlation coefficients are:

For chlorpyrifos:

$$Y = 420.616 * x + 296.404 \quad \text{Corr} = 0.9966$$

For chlorpyrifos **oxon**:

$$Y = 368.0479 * x - 27.656 \quad \text{Corr} = 0.9834$$

### C. Minimum Detection Limit

The minimum detection limit (mdl) is set by the minimum concentration injected (25 **pg/μL**) times the minimum total volume (2.0 **mL**) times the dilution factor (one-half of the sample used). The minimum detectable is 0.10 **μg/sample**.

Assuming a total air sampling rate of 15 lpm for 24 hours, the total air volume processed would be: 21 **m<sup>3</sup>** and the air concentration = 0.10 **μg/21 m<sup>3</sup>** = 4.6 **ng/m<sup>3</sup>**

### Laboratory Recovery Data and Air Collection Efficiency (air trapping) of **Chlorpyrifos** and **Chlorpyrifos oxon**

Laboratory recovery data for chlorpyrifos and chlorpyrifos **oxon** is given in Table 3 and 4 while air collection data for chlorpyrifos run on March 23, 1996 is given in Table 5. A second set of air collection data for chlorpyrifos is given in Table 6. The air collection data for chlorpyrifos **oxon** is given in Table 7.

Table 3. Laboratory Recovery of **Chlorpyrifos** from Resin Spikes

Sample	Fortification (μg)	Recovery (μg)	% Rec	Average	Stddev.
014V50R1	50	48.97	98%		
015V50R2	50	49.56	99%		
016V50R3	50	50.04	100%		
017V50R4	50	49.85	100%		
079V50R5	50	47.92	96%		
080V50R6	50	48.64	97%		
081V50R7	50	48.09	96%	98%	2%
036V0.2R1	0.20	0.19	95%		
037V0.2R2	0.20	0.21	105%		
038V0.2R3	0.20	0.21	105%		
039V0.2R4	0.20	0.18	90%	99%	7%



Table 4. Laboratory Recovery of Chlorpyrifos/Oxon from Resin Spikes <sup>A</sup>

Sample	Fortification (µg)	Parent			Parent Stdev.	Oxon			Oxon Stdev.
		Recovery (µg)	% Rec	Average		Recovery (µg)	% Rec	Average	
082V50R	1 50	51.70	103%			50.56	101%		
083V50R2	50	50.86	102%			52.60	105%		
084V50R3	50	51.43	103%	103%	1%	52.45	105%	104%	2%

A: Recoveries for these samples are averages from two different injections dates.

Table 5. Chlorpyrifos Air Collection Experiments Run on March 23, 1996<sup>A, B, C</sup>

Sample 50 (µg)	Glass Wool (µg)	Primary (µg)	Trapping Efficiency (%)	Total Mass Recovery (%)	Oxon in Primary (µg)	Oxon as Parent (µg)	Sum of P + O (µg)	Trapping Efficiency (%)
Trap Eff. Rep. 1	0.49	40.04	81	81	6.47	6.78	46.82	94
Trap Eff. Rep. 2	0.16	37.10	74	75	7.08	7.42	44.52	89
Trap Eff. Rep. 3	0.25	42.57	86	86	6.18	6.48	49.05	98
Trap Eff. Rep. 4	0.43	42.67	86	86	6.40	6.71	49.38	99

A: Samplers ran for 24 hours @ ca 25 lpm; Maximum temperature 20 °C

B: No chlorpyrifos or chlorpyrifos oxon was found in the back up trap

C: No chlorpyrifos oxon was found on the glass wool samples

"Oxon as Parent" is a molar conversion of the oxon to the parent compound.

"Sum of P + O" is the sum of the converted oxon and the parent found.

"Total Mass Recovery" is = [(Glass wool (µg) + Primary (µg)) × 100]/amt. spiked (µg).

"Trapping Efficiency" is = (Primary (µg) × 100)/(amt. spiked (µg) - amt. recovered on Glass wool)

Table 6. Chlorpyrifos Air Collection Experiments Run on April 30, 1996<sup>A, B, C</sup>

Sample 50 (µg)	Glass Wool (µg)	Primary (µg)	Trapping Efficiency (%)	Total Mass Recovery (%)	Oxon in Primary (µg)	Oxon as Parent (µg)	Sum of P + O (µg)	Trapping Efficiency (%)
Trap Eff. Rep. 1	<0.10	17.38	35	35	19.32	20.25	37.63	75
Trap Eff. Rep. 2	<0.10	17.55	35	35	22.06	23.12	40.67	81
Trap Eff. Rep. 3	<0.10	17.93	36	36	20.58	21.57	39.50	79
Trap Eff. Rep. 4	<0.10	20.38	41	41	19.71	20.65	41.03	82

A: Samplers ran for 24 hours @ ca 25 lpm; Maximum temperature 35 °C

B: No chlorpyrifos or chlorpyrifos oxon was found in the back up trap

C: No chlorpyrifos oxon was found on the glass wool samples

Table 7. Chlorpyrifos Oxon Air Collection Experiments Run on April 30, 1996<sup>A,B, C</sup>

Sample 50 (ug)	Glass Wool (μg)	Primary (μg)	Trapping Efficiency (%)	Total Mass Recovery (%)
Trap Eff. Rep. 1	<0.10	41.10	82	82
Trap Eff. Rep. 2	<0.10	40.14	80	80
Trap Eff. Rep. 3	0.1	32.98	66	66
Trap Eff. Rep. 4	<0.10	34.52	69	69

A: Samplers ran for 24 hours @ ca 25 lpm; Maximum temperature 35 °C

B: No chlorpyrifos or chlorpyrifos oxon was found in the back up trap

C: No chlorpyrifos was found on the glass wool samples

#### Storage Stability

Table 8. Chlorpyrifos Storage Stability Samples <sup>A</sup>

Sample	Fortification (μg)	Recovery (μg)	% Rec	Average	Stdev
002S50R1	50	46.13	92%		
003S50R2	50	44.29	89%		
004S50R3	50	46.27	93%		
005S50R4	50	48.19	96%		
006S50R5	50	44.38	89%	92%	1%

A: 3/24/96-4/30/96 37 Days of Storage in -20 °C Freezer

A Storage Stability Study on Chlorpyrifos Oxon is in Progress.

## APPENDIX II

### LABORATORY REPORT

**Method Development, Ambient Site and Application Site  
Monitoring for Chlorpyrifos and Chlorpyrifos Oxon in Air  
Samples Using XAD-4® Resin as a Trapping Medium**

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Protection Agency

## **DISCLAIMER**

The statements and conclusions in the report are those of the contractor and not necessarily those of the **California** Air Resources Board. The mention of commercial products, their source, or their use in connection with material reported herein is not to be construed as actual or-implied endorsement of such products.

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## I. INTRODUCTION

There have been numerous materials that have been employed as trapping media for the detection of pesticides in air, most significantly: polyurethane foam (PUF), ethylene glycol-impingers, charcoal, glass fiber filters (GFF), and resins. Of the resin mediums that have been used, the XAD" series of resins have proved to be the most beneficial for air sampling for pesticides with diverse ranges of **physicochemical** properties, and sampling durations. **XAD-2®**, **4®**, and **7"** have been preferred for use for air sampling. Of these resins, **XAD-4®**, a 20/50 mesh macro reticular resin, whose structure is a styrene-divinylbenzene copolymer, was selected because of its high surface area, bulk price and ability for trapping chemicals for long periods of sampling.

The objective of the current study is to provide the California Air Resources Board (ARB) with an easy, rapid, sensitive and effective analytical method for the detection of chlorpyrifos and its transformation product, chlorpyrifos **oxon**. This method is appropriate for ambient and application air monitoring for sampling periods of up to 24 hours.

This report addresses five key areas of the chlorpyrifos project: 1) development of an analytical method, 2) trapping efficiencies of air samples using XAD-4" as a trapping medium, 3) ambient site sampling for chlorpyrifos and its transformation product, 4) analysis of samples **from** an application site, and 5) quality assurance samples from the ARB Quality Assurance unit.

## II. ANALYTICAL METHOD

### Analytical Standards

Analytical standards of chlorpyrifos, (Dow Elanco reference number: **MM930503-17**, 99.8% pure) and chlorpyrifos **oxon** (Dow Elanco reference **number:GS-33-82:126**, 95% pure) for use in analysis were obtained directly from Dow Elanco. Shipment of the standards was via overnight service to minimize potential breakdown of standards. Standards were received in May 1996 and were logged into **TAL's** analytical standard repository. Neat standards were kept at -20 °C until the time of use. Stock solutions, 100 **mL** each, 1.0 **mg/mL** concentrations, were prepared using pesticide grade ethyl acetate and kept at 4 °C until the time of use. Dilute spiking and analysis standards were prepared **from** these stock solutions using pesticide grade ethyl acetate.

### Trapping Medium

**XAD-4®** resin (**Rohm** and **Haas**, through Supelco), a macro reticular resin, was employed as the trapping medium for chlorpyrifos and its transformation product. **XAD-4®** along with **XAD-2®** has been used extensively for air sampling of pesticides for sampling

periods as great as 24 hours (References 1, 2). **XAD-4®** resin was prepared prior to use as described in Appendix A.

## **Analytical Method**

### **Laboratory Fortifications**

A preliminary laboratory method validation study was done in March 1996 prior to any air trapping or storage stability experiments, and ambient or application site samples. The method used for the analysis of chlorpyrifos and chlorpyrifos **oxon** was derived from this initial method validation study. With each set of samples (trapping efficiency, storage stability study, ambient site samples, application site samples or quality assurance samples) laboratory spikes were done in triplicate as outlined below. The spiking levels were 0.20  $\mu\text{g}$ , 2.5  $\mu\text{g}$  and 50  $\mu\text{g}/\text{sample}$ .

### **Method**

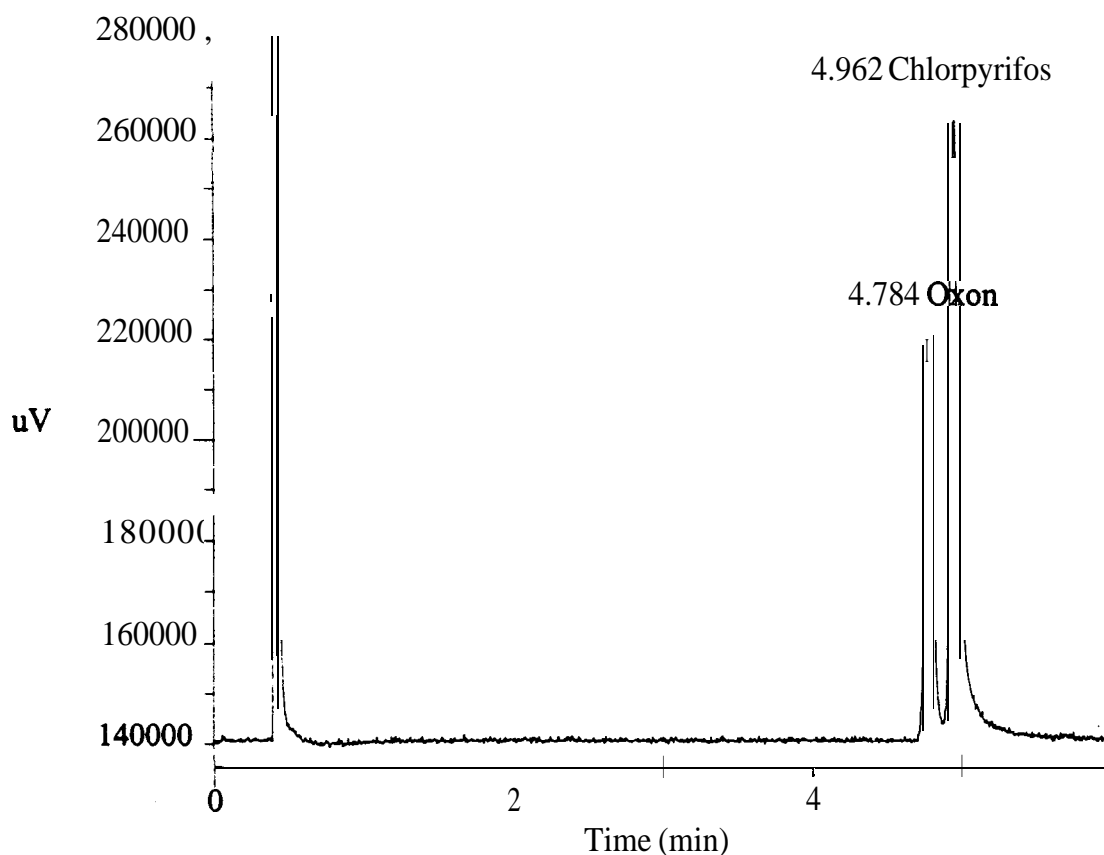
In separate experiments, 0.20 or 50  $\mu\text{g}$  of chlorpyrifos or chlorpyrifos **oxon**, in triplicate, was added to 30 **mL** of resin with a 25  $\mu\text{L}$  syringe and the solvent was allowed to evaporate. 75 **mL** (approximately two bed volumes) of pesticide grade ethyl acetate, or the equivalent, was added to resin sample jars and the jars were swirled for one hour at moderate speed, using a rotary platform shaker. One half of the total volume (37.5 **mL**) was transferred to a 100 **mL** round bottom flask and the ethyl acetate was evaporated just to dryness with a rotary evaporator and a water bath temperature set at approximately 30 °C. The round bottom flask was rinsed with small aliquots (0.3 - 0.5 **mL**) of ethyl acetate, the flask swirled and the sample was quantitatively transferred to a 15 **mL** centrifuge tube. The minimum sample volume was 2.0 **mL**.

### **Analysis**

A Hewlett Packard (HP) Model 5890 Series II gas **chromatograph** equipped with a flame photometric detector (**FPD**) operated in the phosphorus mode (526 **nm** filter), and a HP-CC System Injector-Autosampler (splitless injection) were used to quantitate chlorpyrifos and chlorpyrifos **oxon** during the same chromatographic run. The column used was a 0.53 mm (i.d.) X 30 m Rtx-1 wide bore capillary column (1.5 micron film) (**Restek** Scientific). Data acquisition was accomplished via a **TurboChrom®** (version 4.1) data station (**Perkin Elmer**) and data reductions of the results were performed using an EXCEL® (v. 7.0, Microsoft) spreadsheet program and macro. It should be noted that there may be small discrepancies (<1%) between averages calculated manually from the tabulated data, due to rounding errors, with those numbers generated by the spreadsheets. Parameters

for the analytical instrumentation are listed in Table 1. See Figure 1 for a representative chromatogram.

**Figure 1. 3 $\mu$ L Injection of 400 pg/ $\mu$ L Chlorpyrifos/Chlorpyrifos Oxon on GC-FPD.**



**Table 1. GC Instrument Parameters for Chlorpyrifos/Oxon**

Injector Temp	Detector Temp	Column Temperature (°C)			Flow Rates (mL/min)			
		Initial	Rate	Final	Carrier	Makeup	Air	Hydrogen
250 °C	280 °C	180	10 °C/min	200	20	10	110	75

All samples in an analytical set were quantified by using a **6-point** external linear regression standard curve for both chlorpyrifos and chlorpyrifos **oxon**. Each sample was injected twice and individual standard(s) as well as standard curves were interspersed between samples during each analysis (set). The average of both analyses of each sample was reported. The analysis was based on a linear regression of all the standards injected for that set. It should be noted that all **sample** volumes were adjusted, prior to the actual quantitation, to fit within the limits of the standard curve.

## Limit of Quantitation

The limit of quantitation (LOQ) for the analytical method for both the ambient and application sites was derived from the following:

Minimum detection of the instrument for chlortpyrifos and chlorpyrifos **oxon** is based on the minimum concentration injected that can be consistently quantitated. This quantity, (0.050 **ng/μL**) along with the minimum total volume of the sample and the fact that one-half of the sample is used for the analysis of both compounds. Therefore, the LOQ is:

$$\text{LOQ} = 0.050 \text{ ng/uL} \times 2.0 \text{ mL} \times 2 = 0.20 \text{ } \mu\text{g/sample}$$

The limit of detection was 0.10 **μg/sample**. All samples with responses less than the limit of quantitation, or was not detected, was assigned the value of **<0.20 μg/sample** for both chlorpyrifos and chlorpyrifos **oxon**.

## Recoveries

### Chlorpyrifos

Preliminary recovery data was generated by fortifying four replicates at 50 **μg** each of the **XAD-4®** resin with chlorpyrifos, and four replicates at the limit of quantitation of 0.20 pg. Samples were spiked directly on the resin and the solvent was then allowed to evaporate. Samples were extracted and one-half of each sample was analyzed. Method recoveries for chlorpyrifos are given in Table 2. The average recovery for all replicates of chlorpyrifos was 99 ± 7 percent.

**Table 2. Recovery Data for Fortified Chlorpyrifos on XAD-4® Resin**

Sample I. D.	Fortification (μg)	Recovery (μg)	% Rec	Average	Standard Deviation
014V50R1	50	49.0	98%		
015V50R2	50	49.6	99%		
016V50R3	50	50.0	100%		
017V50R4	50	49.9	100%		
036V0.2R1	0.20	0.19	95%		
037V0.2R2	0.20	0.21	105%		
038V0.2R3	0.20	0.21	105%		
039V0.2R4	0.20	0.18	90%	99%	7%

## Chlorpyrifos Oxon

Resin recovery studies for chlorpyrifos **oxon** were not initiated until May 1, 1996. The average recovery for all replicates of chlorpyrifos **oxon** was  $108 \pm 6$  percent. The results of this study are presented in Table 3.

**Table 3. Preliminary Laboratory Recoveries for Chlorpyrifos Oxon on XAD-4® Resin**

Sample I.D.	Fortification ( $\mu\text{g}$ )	Recovery ( $\mu\text{g}$ )	% Rec	Average	Standard Deviation
082V50R1	50	50.6	101%		
083V50R2	50	52.6	105%		
084V50R3	50	52.5	105%		
088V0.2R1	0.20	0.23	114%		
089V0.2R2	0.20	0.23	117%		
090V0.2R3	0.20	0.21	103%	108%	6%

## Freezer Storage Stability Study

A 37 day storage stability study was initiated for chlorpyrifos on March **24, 1996**, while a 31-day storage stability study for chlorpyrifos **oxon** commenced on April 30, 1996. A total of 20 samples (30 mL resin each) were prepared: 10 resin samples were fortified with 50  $\mu\text{g}$  of chlorpyrifos and an additional 10 resin samples were fortified with 50  $\mu\text{g}$  of chlorpyrifos **oxon**. Four control resin samples were included along with the fortified samples. All samples were stored at  $-20^{\circ}\text{C}$  for the duration of the study. Five of the ten chlorpyrifos and one of the control samples were extracted and analyzed on **4/30/96**, and five of the ten chlorpyrifos **oxon** and one of the control samples were extracted and analyzed on **5/31/96**. The average recovery for chlorpyrifos was  $92 \pm 3$  percent and chlorpyrifos **oxon** was  $100 \pm 1$  percent. There was no apparent conversion of chlorpyrifos to chlorpyrifos **oxon** during the time of storage. The remaining storage stability and control samples were kept in a  $-20^{\circ}\text{C}$  freezer. The results for all replicates, averages and standard deviations are listed in Table 4.

**Table 4. Storage Stability Results for Chlorpyrifos and Chlorpyrifos Oxon**

	Replicates <sup>1</sup>					Average	Std. Dev.
	1	2	3	4	5		
Chlorpyrifos <sup>2</sup>	92	89	93	96	89	92	3
Chlorpyrifos Oxon <sup>3</sup>	101	99	101	101	100	100	1

1: Control samples had <0.20 µg /sample chlorpyrifos and chlorpyrifos oxon.

2: Samples stored at -20 °C for 37 days.

3: Samples stored at -20 °C for 31 days.

### Quality Assurance

While it was not a requirement to follow strict Good Laboratory Practices (GLP) guidelines, quality assurance was kept at a maximum to keep the integrity of the project. Controls (checks, blanks) and fortifications of controls were run with every set. Documentation for the project was at a maximum, including the use of notebooks, instrument logbook and/or computer spreadsheets. All of the necessary components were in place to assure that the study would be reconstructible, a prime requisite for a GLP study.

### Confirmation of Chlorpyrifos and Chlorpyrifos Oxon

The presence or absence of chlorpyrifos and chlorpyrifos **oxon** was qualitatively confirmed for approximately ten percent of the samples using a Hewlett-Packard 6890 gas **chromatograph** coupled to a model 5972A mass selective detector (**MSD**) with Restek Rtx-1 30 m x 0.25 mm (I. D.) column. An HP-GC System Injector-Autosampler was used to inject (splitless mode) samples. The MSD was operated in selective ion monitoring mode (**SIM**), observing the ion fragmentation patterns of 258,286 and 314 for chlorpyrifos and 242,270 and 298 for chlorpyrifos **oxon**. The dwell time for each ion was 100 msec. The limit of detection for the GUMS qualitative data was 25 **pg/µL** for both chlorpyrifos and chlorpyrifos **oxon**. Confirmation criteria included the retention time, as well as the ratio of ions for each compound. The ion ratio was achieved by taking a mass spectra at the apex of the peak. Ion ratios deviation tolerances are usually on the order of 20 percent for the MSD (Reference 3); The parameters for the confirmation gas chromatography are given in Table 5. See Appendix E for sample GC-MSD chromatograms and Appendix F for **confirmation** results.

**Table 5. GC/MS Instrument Parameters for Chlorpyrifos/Oxon Confirmation**

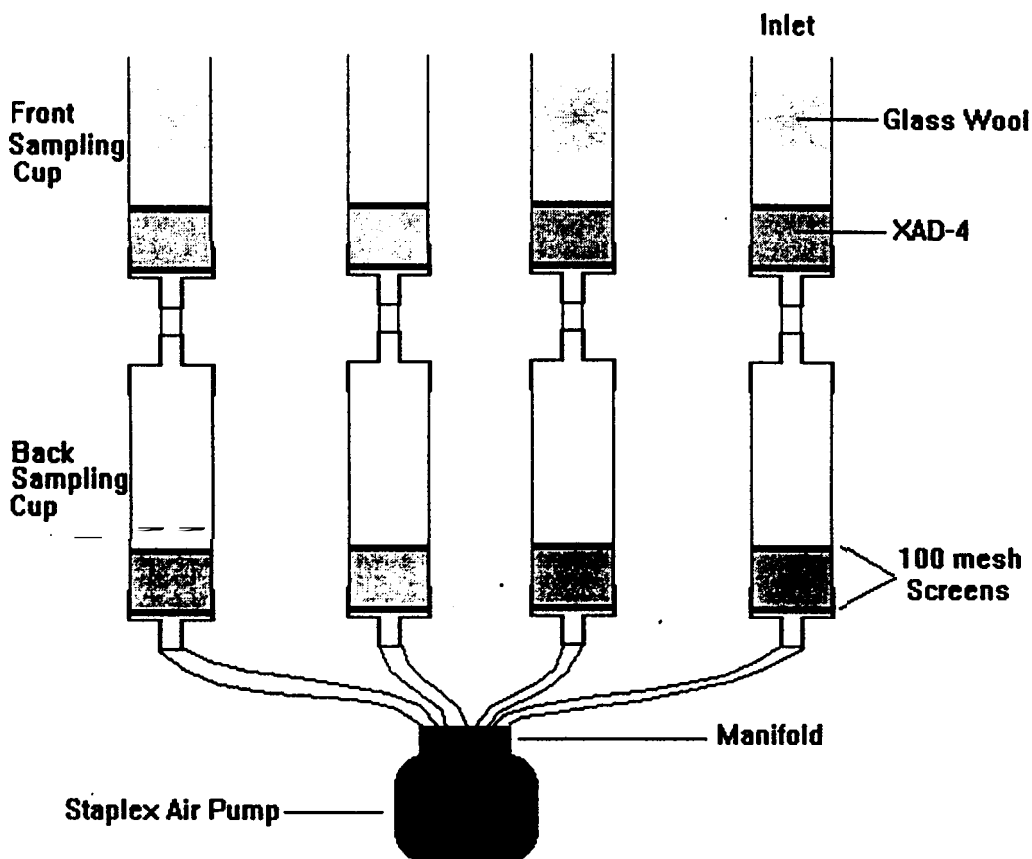
Injector Temp	Detector Temp	Column Temperature (°C)				Carrier Gas (He)
		Initial	Rate	Final	Hold	
250 °C	280 °C	100	20 °C/min	250	2 min	1 mL/min

### III TRAPPING EFFICIENCIES

#### Apparatus

The apparatus used for trapping efficiencies consisted of two 12 cm x 4 cm (id.) Teflon® cartridges (cups), (Savillex Corp). The resin was held in place by installing **100-mesh** stainless steel screens and a Teflon® mesh retainer on each side of the resin inside each cup. The cups were connected in tandem via a **Teflon®** tube (Figure 2) with the top cup, the primary trap, connected to the bottom secondary trap (backup trap). Traps were attached to a one m x 1.2 cm diameter lab rack that made the height of the sampling cups approximately one meter above the sampling surface. The traps were adapted with **Tygon®** tubing (1 cm i.d. x 1 mm wall x 1.25 cm o.d.) and connected the apparatus to a Staplex high volume air sampler fitted with a **5-port** Plexiglass® manifold. Using 30 mL of 20-50 mesh **XAD-4®** resin with this configuration, the **flow rate** for two traps in tandem will be between 25-35 lpm, approximately twice the sampling rate that ARB personnel used in this study. See Figure 2.

**Figure 2. Trapping Efficiency Apparatus**



### **Procedure**

A sampling train was made up with two Teflon sampling cartridges in series. Each cartridge was charged with 30 mL of XAD-4<sup>®</sup> resin, a top Teflon<sup>®</sup> retainer was added to form a sandwich and keep the resin from “vortexing.” Vortexing can cause a “dishing” effect through the build up of resin on the sides and a **thinning** of resin in the center, thus possibly increasing the potential for breakthrough. The backup trap was then attached to the primary trap with a short piece of Teflon<sup>®</sup> tubing. The backup trap also contained a 30 mL resin sandwich.

Acetone washed glass wool was placed above the resin-sandwich in the primary cup and the wool was spiked with either 50  $\mu\text{L}$  of chlorpyrifos or chlorpyrifos **oxon**, using a 1.00  $\mu\text{g}/\mu\text{L}$  solution. The solvent was allowed to evaporate for five minutes prior to turning on the air pumps, so that only the compound of interest remained. Flow rates were measured at the beginning and end of each sampling period.



For chlorpyrifos, two trapping efficiency studies were run on the roof of **the** Environmental Toxicology building. The first study, (Study A), was conducted on March 23-24, 1996, when the average temperature was relatively cool. This study consisted of three parts: 1) Four samplers as described above and one control. The control sample consisted of glass wool, primary and backup traps with XAD-4<sup>®</sup> resin but no compound. 2) **This** part was a primary and backup sampler as described above but **the** chlorpyrifos was spiked directly onto the resin. **The** flow rate was the same for this part. 3) The same as in part 2) only there was no air flow though the sampler for the **24-hour** period. By analyzing the samples **from** 2 and 3, one could ascertain if the glass wool or resin is causing breakdown (oxidation of chlorpyrifos to the corresponding **oxon**) during the sampling period.

The second study, Study B, was conducted for 24 hours on May first and second, where the meteorological parameters of the trapping study would more accurately reflect the meteorological conditions of the actual ambient and application monitoring (**>32 °C** during the daytime sampling period). This set of experiments consisted of the following: Experiment A: Three air samplers fortified with 50 **µg** each of chlorpyrifos and Experiment B: Three air samplers with 50 **µg** each of chlorpyrifos **oxon**. **The** compound of interest was added to the glass wool. Each experiment had its own blank (control) sample consisting of glass wool, primary and backup traps with **XAD-4<sup>®</sup>** resin, but no compound added to the glass wool. All experiments were run for 24-hours. The resin samples were extracted and analyzed as previously described. The glass wool was extracted by swirling **with** ethyl acetate. For these experiments, there were no samples with either chlorpyrifos or the **oxon** applied directly to the resin.

The trapping efficiency can be calculated using the following equation:

$$\% \text{ trapping efficiency} = \frac{\text{Amount trapped} \times 100}{(\text{amt. spiked} - \text{amt. recovered on glass wool}) \times \text{Lab Rec.}}$$

where **the** amount that actually volatilized is the original amount spiked on **the** glass wool minus the amount found on the glass wool after the experiment is completed. The laboratory recovery term of the equation is usually left off for those compounds that exhibit quantitative laboratory recoveries (**> 90%**).

In general, **the** above equation for trapping efficiency works well for compounds **with** vapor pressures within the range of **10<sup>-3</sup>** and **10<sup>-7</sup> torr** and are relatively not polar.

## Results

### Chlorpyrifos

The results of each of the replicates for the Study A, part 1 trapping experiment (March 23-24, 1996, part 1), are given in Table 6. The individual results for the Study B chlorpyrifos experiment, May 1-2, 1996, are given in Table 7. Upon visual inspection of these results it can be seen that: 1) Chlorpyrifos is relatively volatile, only a small amount was left on the glass wool and 2) approximately 96 percent of the amount that is volatilized is actually trapped on the primary resin. For the amount found in the primary trap, 83 percent was as the parent while 13 percent was in the form of the oxon. None of the replicates had chlorpyrifos or oxon breakthrough into the backup trap. The control resin trap did not collect any chlorpyrifos or oxon.

**Table 6. Trapping efficiencies for Chlorpyrifos Conducted During March 23-24, 1996, Part 1.**

Sample	Parent Glass Wool (µg)	Parent Primary (µg)	Parent Backup (µg)	Trapping Efficiency (%)	Total Mass <sup>2</sup> Recovery (%)	Oxon in Primary (µg)	Oxon as <sup>3</sup> Parent (µg)	Sum of s + o (µg)	Trap. Eff. <sup>5</sup> s + o (%)
50 (µg)									
Trap Eff. Rep. 1	0.49	40.0	co.10	81	81	6.47	6.78	46.8	94
Trap Eff. Rep. 2	0.16	37.1	co.10	74	75	7.08	7.42	44.5	89
Trap Eff. Rep. 3	0.25	42.6	co.10	86	86	6.18	6.48	49.1	98
Trap Eff. Rep. 4	0.43	42.7	co.10	86	86	6.40	6.71	49.4	99
Control Resin	co.10	<0.10							

1: Trapping efficiency for parent only.

2: Total mass recovered = (sum glass wool + primary + backup)/amount spiked x 100.

3: The equivalent amount chlorpyrifos oxon as Parent compound.

4: The sum of the chlorpyrifos oxon, as parent, and chlorpyrifos.

5: The total trapping efficiency for parent and oxon.

For the Study A Part 2 experiment, where the sampler with a primary and backup trap in tandem and chlorpyrifos was spiked directly to the resin, 96 percent of the chlorpyrifos was recovered in the primary trap as the parent compound. There was no breakthrough into the backup trap. For Part 3, where the resin was spiked directly but with no air flow, 62% was recovered as chlorpyrifos. There was no chlorpyrifos oxon analysis done for Parts 2 and 3.

For the study that was run during May, complications were observed. Approximately the same amount of mass (S + O) was trapped in the primary trap as was during the March experiments. However, 43 percent of the

chlorpyrifos was converted to chlorpyrifos oxon during the 24-hour experiment. This is more than likely due to the increase in temperature for the experimental period.

**Table 7. Trapping efficiencies for Chlorpyrifos, May 1-2, 1996. Study B, exp. A**

Sample 50 (ug)	Glass Wool (µg)	Primary (µg)	Backup (µg)	Trapping' Efficiency (%)	Total Mass <sup>2</sup> Recovery (%)	Oxon in Primary (µg)	Oxon as' Parent (µg)	sum of s + o (µg)	Trap. Eff. <sup>5</sup> (S + O) (%)
Trap Eff. Rep. 1	co. 10	17.4	co.10	35	35	19.3	20.3	37.6	75.3
Trap Eff. Rep. 2	co. 10	17.6	co.10	35	35	22.1	23.1	40.7	81.3
Trap Eff. <b>Rep. 3</b>	<b>&lt;0.10</b>	17.9	co.10	36	36	20.6	21.6	39.5	79.0
Trap Eff. <b>Rep. 4</b>	co.10	20.4	<b>&lt;0.10</b>	41	41	19.7	20.6	41.0	82.1
Control Resin	co.10	co.10							

1: Trapping efficiency for parent only.

2: Total mass recovered = (sum glass wool + primary + backup)/amount spiked x 100.

3: The equivalent amount chlorpyrifos oxon as parent compound.

4: The sum of the chlorpyrifos oxon, as parent, and chlorpyrifos .

5: The total trapping efficiency for parent and oxon.

### Chlorpyrifos Oxon

Table 8 has the results of the chlorpyrifos oxon trapping study that was conducted on May 1-2, 1996 on the Meyer Hall rooftop (Environmental Toxicology). The average amount trapped was 74 percent with a standard deviation of 8.0 percent and a range of 66 to 82 percent. There was no breakthrough of chlorpyrifos oxon into the backup trap.

**Table 8. Chlorpyrifos Oxon Trapping Efficiencies Results for May 1-2. Study B, exp. B**

Sample	Glass Wool	Primary	Backup	Trapping' Efficiency	Total Mass <sup>2</sup> Recovery
50 (ug)	(ug)	(ug)	(ug)	(%)	(%)
Trap Eff. Rep. 1	co.10	41.1	<0.10	82	a2
Trap Eff. Rep. 2	co.10	40.1	co.10	80	80
Trap Eff. Rep. 3	0.1	33.0	co.10	66	66
Trap Eff. Rep. 4	co.10	34.5	co.10	69	69
Control	co.10	co.10	co.10	-----	-----

1: Trapping efficiency for **oxon** only.

2: Total mass recovered=(sum glass wool + primary + **backup**)/amount spiked x100.

Seiber *et al* in 1989, encountered similar problems with methyl parathion converting to the **oxon** when using the same trapping procedures (Reference 2). Methyl parathion trapping efficiencies were approximately 50% during this study and approximately 50% was converted to methyl parathion **oxon**. Trapping efficiencies were done on a daily basis, on a roof top, during the 1987 rice application season. These results were similar to those found for both chlorpyrifos and chlorpyrifos **oxon**. ‘The authors surmised that, under high temperatures, the glass wool may have the potential to catalyze the transformation of parent organophosphates to their corresponding **oxons**. (Reference 5).

Although not definitively resolved in this project, the data presented indicates that conversion of chlorpyrifos to chlorpyrifos **oxon** may occur if field spikes are fortified “on glass wool” and are “weathered” (ambient air sampling) on hot days. Whereas conversion is decreased if field spikes are fortified “on resin,” even for “hot day” sampling. See QA field spike results.

However, a detailed explanation describing possible routes of the loss of material is beyond the scope of this project contract.

#### IV. AMBIENT AIR SAMPLING

##### Sampling Apparatus

The sampling apparatus for each site consisted of a motorized pump, and tubing connected to a single Teflon® cup that was charged with 30 mL of XAD-4® resin. All sites were installed with primary samplers only and samplers had average flow rates approximately 15 lpm. Sampling durations were on the order of 24 hours. On days selected by ARB personnel, duplicate samples were taken at each site. With the exception of charging the Teflon® air sampling cups with XAD-4® resin, ARB personnel were responsible for all air sampling including set up of the sampling apparatus, sampling procedures, recording of data, and sample shipment to the laboratory.

##### Sample Preparation

Air sample cartridges, for one weeks worth of air sampling, were pre-prepared by TAL personnel with 30 mL of precleaned XAD-4® resin. These cartridges were prepared on the weekend prior to the actual sampling by ARB personnel. Cartridges were charged with resin, capped and stored at ambient temperature until the time they were picked up by ARB personnel.

##### Sample Collection

Ambient sampling commenced on May 28, 1996 and concluded on June 29, 1996. For the most part, each week of sampling had four 24-hour periods which were chosen at ARE3 personnel's discretion. All samples were kept in the field until the time of delivery to TAL personnel. In general, samples were received on the completion of the last sampling day of the week.

##### Sample Storage

All samples were kept on dry ice from the time of sampling to the time the samples were received by the laboratory. Samples were boxed and placed in ice chests packed with dry ice and transported directly to the laboratory at the end of the sampling week by ARB personnel.

## Analysis of Sets

Upon receipt of the samples, samples were logged into an Excel spreadsheet with the ARB identification and log number. Also, each sample was given a unique TAL identification number. All of the sample jar labels were checked against the chain of custody. To insure the minimum of potential conversion and/or degradation, all samples were worked up on the evening they were received and analyzed within 24 hours of extraction. Laboratory fortification samples, in triplicate, were prepared by adding 30 mL of **XAD-4®** resin to the same type of jars that the ambient samples were in. The fortifications ranged from 0.2 to 50 **µg/sample** each, for chlorpyrifos and chlorpyrifos **oxon**. A laboratory control resin sample, consisting of 30 mL of **XAD-4®** resin, was included with each set analyzed. The analysis for chlorpyrifos and chlorpyrifos **oxon** was completed within 48 hours of sample receipt.

## Results

### **Chlorpyrifos**

A daily summary of the chlorpyrifos detected in each sample for each site is presented in Table 9. A graph of the daily chlorpyrifos concentration is presented in Figure 3. For chlorpyrifos **oxon**, a daily summary of the residues detected in each sample for each site is presented in Table 10. A graph of the daily chlorpyrifos **oxon** concentration is presented in Figure 4. Results of all individual samples are given in Appendix C.

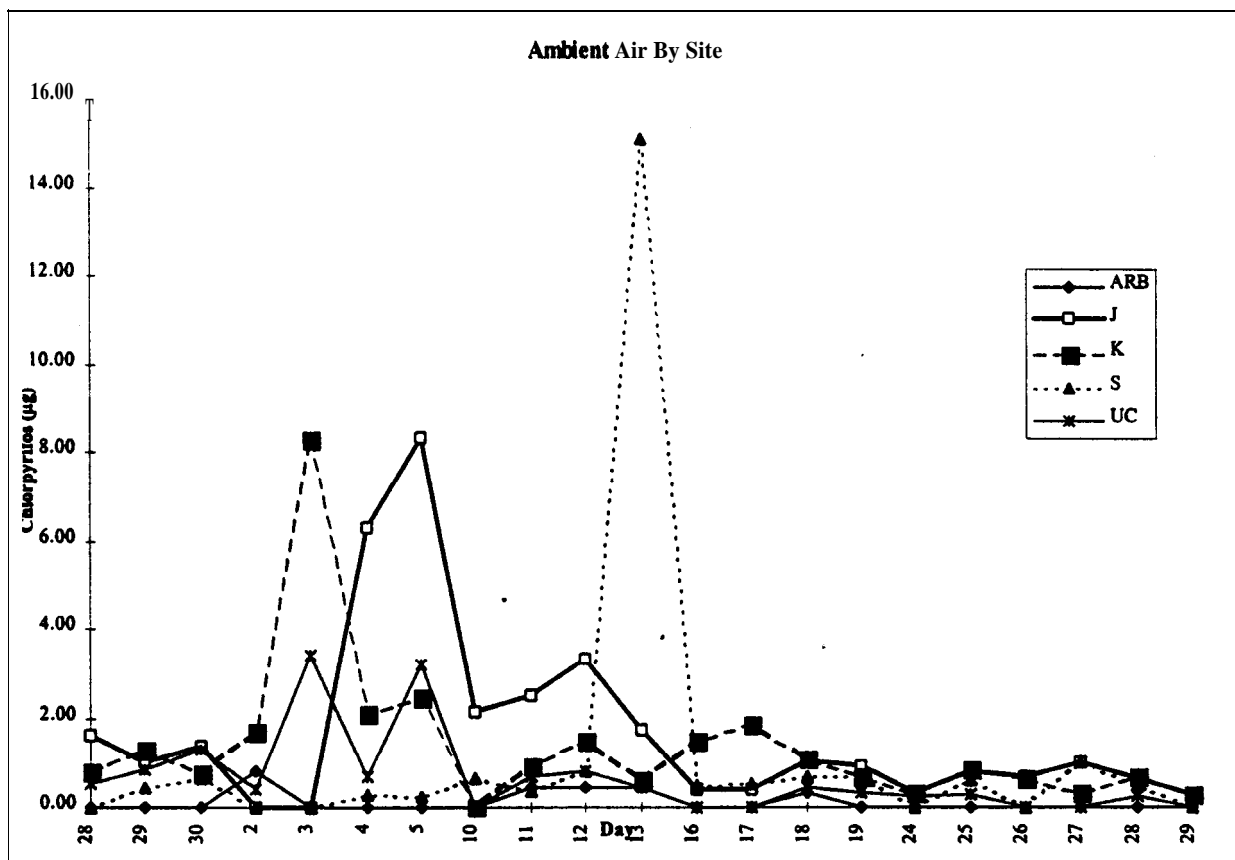
**Table 9. Summary of Ambient Site Chlorpyrifos Results (µg/sample)**

Sampling Period	Ambient Sampling Site <sup>1</sup>				
	ARB	J	K	S	UC
5/28/96	<0.20	1.63	0.81	<0.20	0.54
5/29/96	<0.20	1.00	1.01	0.43	0.86
5/30/96	<0.20	1.37	0.78	0.66	1.29
6/2/96	0.79	<0.20	1.69	<0.20	0.42
6/3/96	<0.20	<0.20	8.27	<0.20	3.40
6/4/96	<0.20	6.30	2.1	0.30	0.68
6/5/96	<0.20	8.33	2.45	0.26	3.20
6/10/96	<0.20	2.15	- <sup>2</sup>	0.64	- <sup>2</sup>
6/11/96	0.46	2.52	0.92	0.37	0.70
6/12/96	0.44	3.33	1.51	0.80	0.82
6/13/96	0.46	1.75	0.62	15.1	0.45
6/16/96	<0.20	0.39	1.48	0.47	<0.20
6/17/96	<0.20	0.39	1.84	0.52	<0.20
6/18/96	0.33	1.07	1.10	0.69	0.45
6/19/96	<0.20	0.93	0.69	0.70	0.32
6/24/96	<0.20	0.32	0.32	<0.20	0.23
6/25/96	<0.20	0.79	0.86	0.60	0.30
6/26/96	<0.20	0.69	0.63	<0.20	<0.20
6/27/96	<0.20	1.02	0.31	1.03	<0.20
6/28/96	<0.20	0.65	0.69	0.48	0.24
6/29/96	<0.20	0.28	0.29	<0.20	<0.20

1: Values for duplicate samples were averaged.

2: No sample sent to the laboratory

**Figure 3. Ambient Site Results for Chlorpyrifos (May 28-June 29).**



### Chlorpyrifos Oxon

A daily summary of the chlorpyrifos **oxon** detected in each sample for each site is presented in Table 10 and Figure 4.



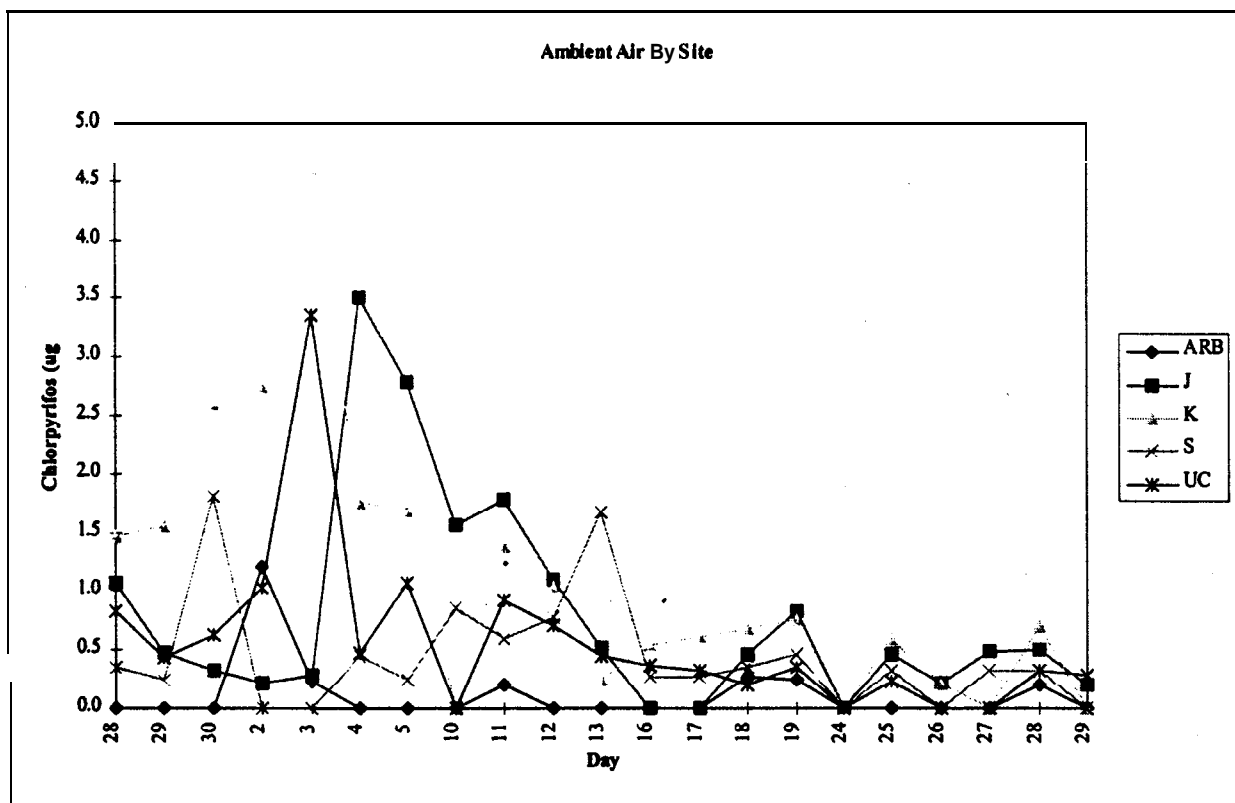
**Table 10. Summary of Ambient Site Chlorpyrifos Oxon Ambient Site Results (µg/sample)**

Sampling Period	Ambient Sampling Site"				
	ARB	J	K	S	UC
5/28/96	<0.20	1.07	1.47	0.36	0.83
5/29/96	<0.20	0.46	1.55	0.24	0.47
5/30/96	<0.20	0.32	2.60	1.81	0.62
6/2/96	1.21	0.22	2.74	<0.20	1.03
6/3/96	0.23	0.29	4.61	<0.20	3.53
6/4/96	<0.20	3.50	1.75	0.45	0.47
6/5/96	<0.20	2.79	1.68	0.24	1.07
6/10/96	<0.20	1.56	- <sup>2</sup>	0.86	- <sup>2</sup>
6/11/96	0.20	1.78	1.38	0.60	0.92
6/12/96	<0.20	1.10	1.05	0.78	0.71
6/13/96	<0.20	0.51	0.25	1.67	0.45
6/16/96	<0.20	<0.20	0.54	0.27	0.37
6/17/96	<0.20	<0.20	0.61	0.27	0.33
6/18/96	0.27	0.46	0.68	0.36	0.21
6/19/96	0.24	0.83	0.76	0.46	0.35
6/24/96	<0.20	<0.20	<0.20	<0.20	<0.20
6/25/96	<0.20	0.46	0.59	0.32	0.23
6/26/96	<0.20	0.22	0.22	<0.20	<0.20
6/27/96	<0.20	0.49	<0.20	0.33	<0.20
6/28/96	0.21	0.50	0.70	0.32	0.32
6/29/96	<0.20	0.20	<0.20	<0.20	0.29

1: Values for duplicate samples were averaged.

2: No sample sent to the laboratory.

**Figure 4. Ambient Site Results for Chlorpyrifos Oxon (May 28-June 29)**



### Quality Assurance

All fortified **XAD-4®** resin laboratory check samples gave reasonable recoveries for both chlorpyrifos and chlorpyrifos **oxon**. The recovery for chlorpyrifos laboratory/ambient validation samples was **from** 91% to 109% with an average recovery of 99% and a standard deviation of 5% (n = 30). For chlorpyrifos **oxon** the laboratory/ambient recovery range was **from** 85% to 117% with an average recovery of 100% with a standard deviation of 7% with (n = 33). The results of all laboratory validation samples, listed by week, are given in Appendix B.

Table 11 has the results for the concurrent laboratory resin fortification samples run with each set of ambient samples.

**Table 11. Average Laboratory Fortification Recovery for Ambient Site Analysis**

Fortification Level ( $\mu\text{g}$ )	# Replicates	Chlorpyrifos (% Recovery)		Chlorpyrifos Oxon (% Recovery)	
		Average	Standard Deviation	Average	Standard Deviation
0.20	6	101	5	107	7
2.5	18	97	5	98	7
50	9	101	5	99	6

**UCD - Field Spikes**

The objective of this study was to determine the amount, if any, of chlorpyrifos converted to chlorpyrifos **oxon** once the resin had trapped the parent compound. Therefore, these samples were fortified only with chlorpyrifos. Field spikes, five replicates, were prepared by TAL personnel on 6/20/96, using the following procedure. In order to properly assess small conversions, resin spikes were prepared by the addition of 500  $\mu\text{L}$  of a 100  $\mu\text{g/mL}$  chlorpyrifos standard directly onto 30  $\text{mL}$  of **XAD-4<sup>®</sup>** resin that had been placed in Teflon air sampling cups. The sampling cups that included the spiked resin, were capped then placed in a cooler that contained dry ice. ARB personnel transported the fortified samples to the ARB ambient sampling site where one sample each period was collocated and run concurrently with the **ARB** air sampler. The average recovery for chlorpyrifos was  $94 \pm 6$  percent. The average percent conversion to the corresponding **oxon** was  $2 \pm 1$  percent. The results are presented in Table 12.

**Table 12. UC Davis Ambient Field Spikes**

Sample I. D.	ARB Log #	Chlorpyrifos ( $\mu\text{g}$ )	Recovered (%)	Chlorpyrifos Oxon ( $\mu\text{g}$ )	Percent Conversion
FAUCD-1	106	45.4	91	1.2	3
FAUCD-2	112	52.0	104	0.7	1
FAUCD-3	119	47.1	94	0.5	1
FAUCD-4	129	45.1	90	2.0	4
FAUCD-5	135	46.5	93	1.1 <sup>A</sup>	3

A: There was 0.21  $\mu\text{g}$  chlorpyrifos oxon found in the regular ARB-20 sample

### ARB Field and Trip Spikes

A second set of field spikes were initiated in mid-June by ARB Staff. These samples also were transported to the field and had air drawn through them at the background site, and were returned to the TAL laboratory for analysis. The results for this study are given in Table 13. The results of a third set of trip spikes are presented in Table 14. These samples were “non-weathered” trip spikes: samples that were fortified in the laboratory, taken to the field and returned to the laboratory without having any air drawn through them.

**Table 13. ARB Ambient Field and Trip Spikes**

Sample I. D.	Corresponding Ambient Sample	Parent <sup>A</sup> Recovery (µg)	Average <sup>B</sup> Ambient (µg)	Net <sup>C</sup> (µg)	Oxon <sup>D</sup> Recovery (µg)	Average <sup>E</sup> Ambient (µg)	Net <sup>F</sup> (µg)
QA1A	ARB-12	4.89	<0.20	4.89	5.54	<0.20	5.54
QA2A	ARB-13	1.02	<0.20	1.02	<0.20	<0.20	-
QA3A	ARB-14, ARB-14D	1.09	.032	0.77	0.24	0.34	-
QA4A	ARB-15	136	<0.20	136	23.7	0.24	23.5
QA5A	ARB-15	46.0	<0.20	46.0	76.4	0.24	76.2

A: Chlorpyrifos analysis, average of two analysis.

B: Chlorpyrifos residue in the collocated ARB site sample.

C: Net Chlorpyrifos residue determined by chlorpyrifos recovery minus chlorpyrifos at ambient site.

D: chlorpyrifos **oxon** analysis, average of two analysis.

E: Chlorpyrifos **oxon** residue in the collocated ARB site sample.

F: Net Chlorpyrifos **oxon** residue determined by chlorpyrifos recovery minus **chlorpyrifos** at ambient site.

**Table 14. ARB Ambient Trip Spike Results**

Sample I. D.	Ave. Parent Recovery (µg)	Ave. Oxon Recovery (µg)
QA1B	4.64	2.19
QA2B	1.96	1.69
QA3B	0.98	<0.20
QA4B	1.47	<0.20
QA5B	0.22	1.44

## **V. APPLICATION SITE MONITORING**

### **Sampling Apparatus**

The sampling apparatus for each site consisted of a motorized pump, and tubing connected to a single Teflon cup that was charged with 30 mL of XAD-4® resin. All sites were installed with primary samplers only and samplers had average flow rates approximately 15 lpm. With the exception of charging the Teflon air sampling cups with XAD-4® resin, ARJ3 personnel were responsible for all air sampling including set up of the sampling apparatus, sampling procedures, recording of data, and sample shipment to the laboratory.

### **Sample Preparation**

Air sample cartridges, for one weeks worth of air sampling, were pre-prepared by TAL personnel with 30 mL of precleaned XAD-4® resin. These cartridges were prepared on the weekend prior to the actual sampling by TAL personnel. Cartridges were charged with resin, capped and stored at ambient temperature until the time they were picked up by ARB personnel.

### **Sample Collection**

Ambient sampling for Application Site commenced on June 2, 1996 and concluded on June 6, 1996. All samples were kept in the field until the time of delivery to TAL personnel. In general, samples were received on the completion of the last sampling day of the week.

### **Sample Storage and Shipment**

All samples were kept on dry ice **from** the time of sampling to the time the samples were received by the laboratory. Samples were boxed and placed in ice chests packed with dry ice and transported directly to the laboratory at the end of the, sampling week by ARB personnel.

### **Analysis of Sets**

Upon receipt of the samples, samples were logged into an Excel spreadsheet **with** the ARB identification and log number. Also, each sample was given an unique TAL identification number. All of the sample jar labels were checked against the chain of custody. To insure the minimum of potential conversion and/or degradation, all samples were worked up on the evening they were received and analyzed within 24 hours of extraction. Laboratory fortification samples, in

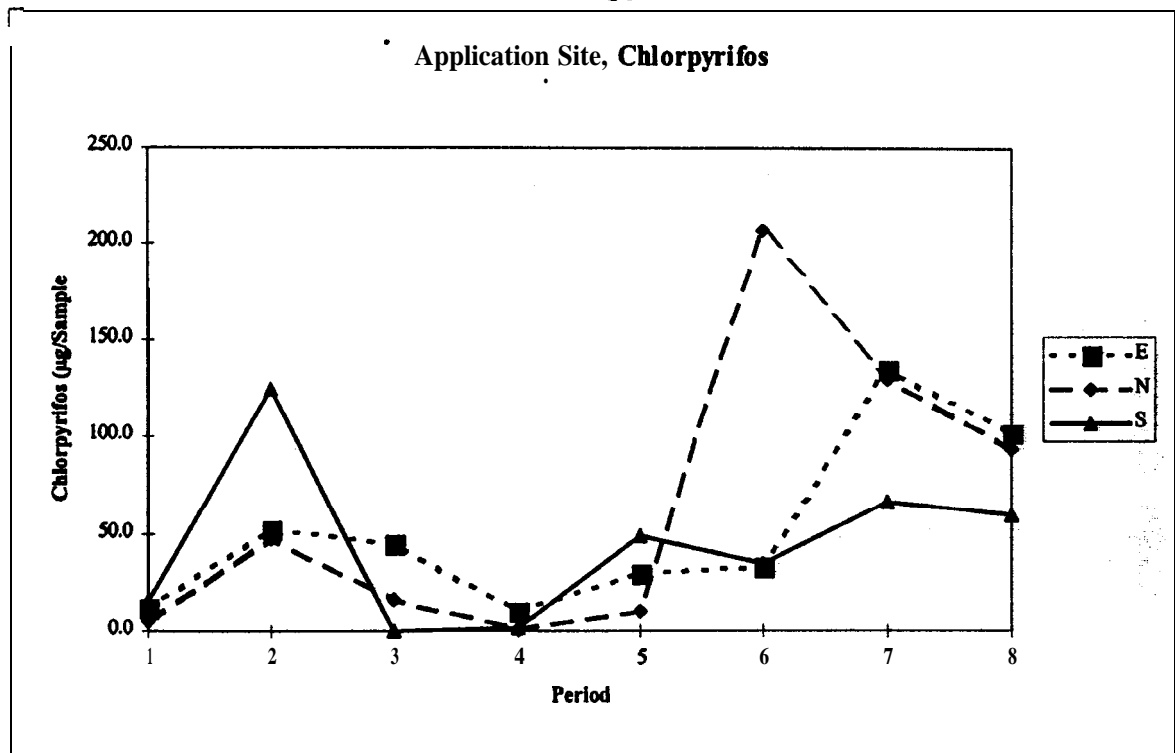
triplicate, were prepared by adding 30 mL of XAD-4<sup>®</sup> resin to the same type of jars that the ambient samples were in. The fortifications ranged from 0.2 to 50 µg/sample each, for chlorpyrifos and chlorpyrifos oxon. A laboratory control resin sample, consisting of 30 mL of XAD-4<sup>®</sup> resin, was included with each set analyzed. The analysis for chlorpyrifos and chlorpyrifos oxon was completed within 48 hours of sample receipt.

## Results

### Application Site Samples

Chlorpyrifos and chlorpyrifos oxon results may be found in Appendix C. A graph of the chlorpyrifos concentration for a given sampling period is given in Figure 5.

**Figure 5. Application Site Results for Chlorpyrifos.**



### Trip Spikes

Four trip spikes were prepared by ARB staff. The trip spikes were prepared by fortifying four 30 mL resin blank samples with an unknown quantity of chlorpyrifos and chlorpyrifos oxon. The fortification of the resin was carried out by ARB personnel and the levels of the fortifications were not disclosed to TAL personnel until after completion of analysis. Samples were kept on dry ice and transported to the application site area. The trip spikes were sent back to the laboratory for analysis along with the first and second period application samples on June 7, 1996 (Table 15).

### Trip Spike Results

The results for the individual trip spikes are given in Table 15. The percent average recovery for the four chlorpyrifos samples was 99% with a standard deviation of < 1% while the percent recovery for chlorpyrifos oxon was 99% and a standard deviation of 4%.

**Table 15. Application Site Trip Spike Results ( $\mu\text{g}/\text{sample}$ )**

Sample I. D.	Fortification ( $\mu\text{g}$ )	Chlorpyrifos Detected ( $\mu\text{g}$ )	Recovery (%)	Fortification ( $\mu\text{g}$ )	Oxon Detected ( $\mu\text{g}$ )	Recovery (%)
S040-01	500	491	98		0.21 <sup>A</sup>	
S040-02	250	247	99	25.0	25.7	103
S040-03	100	98.7	99	100	96.2	96
S040-04		B		250	245	98
178C <sup>C</sup>	n. d.	<0.20		n. d.	<0.20	

A: Oxon residue is probably due to a trace amount of the oxon in the chlorpyrifos standard.

B: Chlorpyrifos oxon concentration too high to determine significant quantity of chlorpyrifos.

C: Sample 178C was a laboratory control resin sample.



## VI. ARB QUALITY ASSURANCE

Additional quality assurance were samples prepared by ARB Staff, and were analyzed by TAL personnel on July 22, 1996. The results of these analyses and the results of three TAL laboratory fortifications analyzed on the same day are given in Table 16.

**Table 16. ARB Quality Assurance Sample Results.**

Sample	ARB	Chlorpyrifos (µg)	Chlorpyrifos (µg)	Error (%)	Oxon (µg)	Oxon (µg)	Error (%)
Number	Number	Fortified	Found		Fortified	Found	
310V2.5R16 <sup>1</sup>		2.50	2.28	9	2.50	2.12	15
311V2.5R17 <sup>1</sup>		2.50	2.59	4	2.50	2.57	3
312V2.5R18 <sup>1</sup>		2.50	2.70	8	2.50	2.72	9
309C	Control	0	<0.20		0	<0.20	
313 <sup>2</sup>	QA-1C	UNK <sup>3</sup>	5.04	NA <sup>4</sup>	UNK <sup>3</sup>	1.21	NA <sup>4</sup>
314 <sup>2</sup>	QA-2C	UNK <sup>3</sup>	5.33	NA <sup>4</sup>	UNK <sup>3</sup>	1.12	NA <sup>4</sup>
315 <sup>2</sup>	QA-3C	UNK <sup>3</sup>	2.96	NA <sup>4</sup>	UNK <sup>3</sup>	<0.20	NA <sup>4</sup>
316 <sup>2</sup>	QA-4C	UNK <sup>3</sup>	200.12	NA <sup>4</sup>	UNK <sup>3</sup>	20.16	NA <sup>4</sup>
317 <sup>2</sup>	QA-5C	UNK <sup>3</sup>	5.05	NA <sup>4</sup>	UNK <sup>3</sup>	1.29	NA <sup>4</sup>
318 <sup>2</sup>	QA-1L	UNK <sup>3</sup>	5.82	NA <sup>4</sup>	UNK <sup>3</sup>	2.80	NA <sup>4</sup>
319 <sup>2</sup>	QA-2L	UNK <sup>3</sup>	1.08	NA <sup>4</sup>	UNK <sup>3</sup>	<0.20	NA <sup>4</sup>
320 <sup>2</sup>	QA-3L	UNK <sup>3</sup>	5.41	NA <sup>4</sup>	UNK <sup>3</sup>	3.01	NA <sup>4</sup>
321 <sup>2</sup>	QA-4L	UNK <sup>3</sup>	1.01	NA <sup>4</sup>	UNK <sup>3</sup>	<0.20	NA <sup>4</sup>
322 <sup>2</sup>	QA-5L	UNK <sup>3</sup>	<0.20	NA <sup>4</sup>	UNK <sup>3</sup>	<0.20	NA <sup>4</sup>
323 <sup>2</sup>	QA-6L	UNK <sup>3</sup>	10.36	NA <sup>4</sup>	UNK <sup>3</sup>	<0.20	NA <sup>4</sup>
324 <sup>2</sup>	QA-7L	UNK <sup>3</sup>	9.95	NA <sup>4</sup>	UNK <sup>3</sup>	5.51	NA <sup>4</sup>
325 <sup>2</sup>	QA-8L	UNK <sup>3</sup>	23.48	NA <sup>4</sup>	UNK <sup>3</sup>	4.94	NA <sup>4</sup>
326 <sup>2</sup>	QA-9L	UNK <sup>3</sup>	24.58	NA <sup>4</sup>	UNK <sup>3</sup>	10.68	NA <sup>4</sup>
327 <sup>2</sup>	QA-10L	UNK <sup>3</sup>	50.99	NA <sup>4</sup>	UNK <sup>3</sup>	53.71	NA <sup>4</sup>

1: TAL Laboratory fortification samples

2: ARB QA Samples

3: Unknown

4: Not Applicable

## VII. PROJECT CONCLUSIONS

A method for chlorpyrifos and its transformation product, chlorpyrifos **oxon**, was developed for air samples using **XAD-4®** as a trapping medium. Laboratory recovery data for both compounds were quantitative. The average laboratory recovery for chlorpyrifos was  $99 \pm 5$  percent while the average laboratory recovery for chlorpyrifos **oxon** was  $100 \pm 7$  percent

Results of two air trapping studies concluded the following: 1) At a flow rate of approximately 30 L/min for 24 hours, no breakthrough was observed for **chlorpyrifos/chlorpyrifos oxon** in the backup traps, either at moderate temperature (approximately 20°C), or at higher temperature (approximately 35 °C, the temperature of the air and Environmental Toxicology's roof top for trapping study done on May 1, 1996). 2) For the trapping efficiency study at low temperature where a glass wool plug was spiked, the uncorrected recovery for total chlorpyrifos was 95 percent with 82 percent as the parent and 13 percent as the **oxon**. 3) The quantity of **oxon** formed when resin was fortified directly and air pulled through it for 24 hours at 30 mL/min was less than 3.0 percent. 4) For the trapping efficiency study at high temperature where a glass wool plug was spiked, the trapping efficiency was 79 percent with 36 percent in the form of the parent and 43 percent in the form of the **oxon**. 5) For the parent compound, the total average mass (the sum of the residue of the parent plus the **oxon**) recovered from spiked air samples ranged from 75 to 98%. 6) Air trapping efficiency experiments, at optimal conditions for this study (approximately 35°C), concluded that approximately 79% of the potential vaporized compound would be trapped by this method, and is comparable to other compounds with similar vapor pressures and polarities.

Samples from an ambient site study, collected by **ARB** personnel, were analyzed within 48-hours of receipt. For the ambient site study, 92 out of 210 total samples had chlorpyrifos residues which were above the limit of quantitation of 0.20 micrograms/sample. There were 90 positive responses for chlorpyrifos **oxon** above the limit of quantitation.

For the application site, chlorpyrifos and chlorpyrifos **oxon** were both detected above the limit of quantitation for all samples taken.

Quality assurance was kept to a maximum during the project by running three fortifications with each set of samples analyzed. Also, the ARB Quality Assurance Unit submitted blind-fortified samples for analysis.

## **ACKNOWLEDGMENTS**

We wish to acknowledge the technical assistance of Cindy Castronovo, Kevin Mongar, Steve **Nunn**, Don Fitzell, and Gloria Lindner with the California Air Resources Board, and Bronson Hung with the Department of Environmental Toxicology for their technical assistance. This study was supported by contract funds **from** the **California** Air Resources Board. Mention of proprietary products is made for identification purposes only and does not imply endorsement by ARB.

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## APPENDICIES

### Appendix A. Preparation of XAD-4® Resin

1. Add ~ 16 liters of XAD-4 resin to a 61 x 29 cm cylindrical **Pyrex container** (~ 40 L).
2. Wet the resin with one gallon of methanol (Resi-grade or equivalent. [Caution: The resin will expand in the presence of organic solvents. This prevented rapid expansion of the resin]).
3. Remove fines by overfilling the container with deionized water with the hose placed at the bottom of the container and stirred vigorously.
4. Two liters of 0.25 N hydrochloric acid was added and stirred for 30 minutes.
5. Add water and vacuum off fines and water with an apparatus prepared with stiff tube covered at the inlet end with gauze and the outlet end connected to a large trap.
6. The container was re-filled with DI water **and** stirred.
7. Steps **#5** and 6 were repeated until the water above the resin was clear and the **pH** is that of the deionized water.
8. Transfer cleaned resin to 1 gallon containers and store in methanol.
9. Transfer resin to a large Soxlet extractor and extract resin with methanol for 24 hours.
10. Add fresh methanol and extract for another 24 hours.
11. Extract resin with ethyl acetate for 24 hours. Add fresh ethyl acetate and extract for an additional 24 hours.
12. Dry the resin in a vacuum oven (25 in. Hg) for 3-4 days at **65°C** or until all trace of ethyl acetate is gone from the resin.
13. Store resin in clean dry jars with Teflon® lined lids. Store at room temperature until , time of use.

## Appendix B. TAL Laboratory Fortifications Results for Chlorpyrifos and Chlorpyrifos Oxon

Sample I.D.	Sample Date	Fortification Level (µg)	Chlorpyrifos Recovery				Chlorpyrifos Oxon Recovery			
			Amount (µg)	Percent (%)	Average (%)	St. Dev. (%)	Amount (µg)	Percent (%)	Average (%)	St. Dev. (%)
088V0.2R1	5/31/93	0.20	0.21	106%			0.23	114%		
089V0.2R2	5/31/93	0.20	0.21	107%			0.23	117%		
090V0.2R3	5/31/93	0.20	0.19	94%			0.21	103%		
114V0.2R4	6/7/96	0.20	0.20	100%			0.20	100%		
115V0.2R5	6/7/96	0.20	0.20	101%			0.22	109%		
116V0.2R6	6/7/96	0.20	0.19	96%	101%	5%	0.20	101%	107%	7%
179V2.5R1	6/7/96	2.5	2.54	102%			2.61	104%		
180V2.5R2	6/7/96	2.5	2.44	97%			2.47	99%		
181V2.5R3	6/7/96	2.5	2.54	102%			2.62	105%		
212V2.5R4	6/14/96	2.5	2.42	97%			2.45	98%		
213V2.5R5	6/14/96	2.5	2.59	104%			2.62	105%		
214V2.5R6	6/14/96	2.5	2.38	95%			2.33	93%		
256V2.5R7	6/21/96	2.5	8.68	A			2.37	95%		
257V2.5R8	6/21/96	2.5	4.77	A			2.44	98%		
258V2.5R9	6/21/96	2.5	5.12	A			2.74	110%		
260V2.5R10	6/28/96	2.5	2.31	92%			2.33	93%		
261V2.5R11	6/28/96	2.5	2.38	95%			2.33	93%		
262V2.5R12	6/28/96	2.5	2.40	96%			2.37	95%		
305V2.5R13	7/1/96	2.5	2.33	93%			2.31	92%		
306V2.5R14	7/1/96	2.5	2.28	91%			2.19	88%		
307V2.5R15	7/1/96	2.5	2.27	91%			2.30	92%		
310V2.5R16	7/22/96	2.5	2.28	91%			2.12	85%		
311V2.5R17	7/22/96	2.5	2.59	104%			2.57	103%		
312V2.5R18	7/22/96	2.5	2.70	108%	97%	5%	2.72	109%	98%	7%
082V50R1	5/1/96	50	51.7	103%			50.6	101%		
083V50R2	5/1/96	50	50.9	102%			52.6	105%		
084V50R3	5/1/96	50	51.4	103%			52.5	105%		
183V50R4	6/8/96	50	46.7	93%			48.8	98%		
184V50R5	6/8/96	50	50.1	100%			50.7	101%		
185V50R6	6/8/96	50	47.7	95%			48.2	96%		
216V50R7	6/20/96	50	54.3	109%			50.7	101%		
217V50R8	6/20/96	50	51.0	102%			49.3	99%		
218V50R9	6/20/96	50	49.5	99%	101%	5%	43.1	86%	99%	6%

A: Chlorpyrifos data not reported due to resin contamination, oxon data is unaffected.

### Appendix C. Ambient Site Individual Results for Chlorpyrifos and Chlorpyrifos Oxon

Trace Analytical Laboratory		Air Resources Board			Chlorpyrifos µg/sample	Chlorpyrifos Oxon µg/sample
Receiving Date	Sample I. D.	Sample Date	Sample I. D.	Log #		
5/31/96	92	5/28/96	ARB-01	1	<0.20	<0.20
5/31/96	93	5/28/96	J-01	2	1.63	1.07
5/31/96	94	5/28/96	S-1	3	<0.20	0.36
5/31/96	95	5/28/96	K-1	4	0.81	1.47
5/31/96	96	5/28/96	UC-1	5	0.54	0.83
5/31/96	97	5/29/96	ARB-02	6	<0.20	<0.20
5/31/96	98	5/29/96	ARB-02D	7	<0.20	<0.20
5/31/96	99	5/29/96	J-02	8	1.00	0.47
5/31/96	100	5/29/96	J-02D	9	1.00	0.45
5/31/96	101	5/29/96	S-2	10	0.41	0.23
5/31/96	102	5/29/96	S-2D	11	0.45	0.24
5/31/96	103	5/29/96	K-2	12	1.02	1.54
5/31/96	104	5/29/96	K-2D	13	1.55	0.99
5/31/96	105	5/29/96	UC-2	14	0.83	0.49
5/31/96	106	5/29/96	UC-2D	15	0.89	0.44
5/31/96	108	5/30/96	ARB-03	17	<0.20	<0.20
5/31/96	109	5/30/96	J-03	18	1.37	0.32
5/31/96	110	6/4/96	S-3	19	0.66	1.81
5/31/96	111	5/30/96	K-3	20	0.78	2.60
5/31/96	112	5/30/96	UC-3	21	1.29	0.62
6/6/96	117	6/2/96	ARB-04	23	0.79	1.21
6/6/96	118	6/2/96	K-1	24	1.69	2.74
6/6/96	119	6/2/96	S-1	25	<0.20	<0.20
6/6/96	120	6/2/96	J-04	26	<0.20	0.22
6/6/96	121	6/2/96	UC-1	27	0.42	1.03
6/6/96	122	6/3/96	ARB-05	28	<0.20	0.23
6/6/96	123	6/3/96	K-2	29	8.27	4.61
6/6/96	124	6/3/96	S-2	30	<0.20	<0.20
6/6/96	125	6/3/96	J-05	31	<0.20	0.29
6/6/96	126	6/3/96	UC-2	32	3.40	3.53
6/6/96	127	6/4/96	ARB-06	33	<0.20	<0.20
6/6/96	128	6/4/96	K-3	34	2.10	1.75
6/6/96	129	5/30/96	S-3	35	0.30	0.45
6/6/96	130	6/4/96	J-06	36	6.30	3.50
6/6/96	131	6/4/96	UC-3	37	0.68	0.47
6/6/96	132	6/5/96	ARB-07	38	<0.20	<0.20
6/6/96	133	6/5/96	ARB-07D	39	<0.20	<0.20
6/6/96	134	6/5/96	K-4	40	2.50	1.71
6/6/96	135	6/5/96	K-4D	41	2.40	1.64

### Appendix C. Ambient Site Individual Results for Chlorpyrifos and Chlorpyrifos Oxon (Cont.)

Trace Analytical Laboratory		Air Resources Board			Chlorpyrifos µg/Sample	Chlorpyrifos Oxon µg/Sample
Receiving Date	Sample I. D.	Sample Date	Sample I. D.	Log #		
6/6/96	136	6/5/96	S-4	42	0.30	0.27
6/6/96	137	6/5/96	S-4D	43	0.21	0.21
6/6/96	138	6/5/96	J-07	44	8.77	3.04
6/6/96	139	6/5/96	J-07D	45	7.89	2.53
6/6/96	140	6/5/96	UC- 4	46	3.24	1.07
6/6/96	141	6/5/96	UC-4D	47	3.15	1.06
6/14/96	187	6/10/96	ARB-08	45	co.20	co.20
6/14/96	188	6/10/96	J-8	46	2.15	1.56
6/14/96	189	6/10/96	S-8	47	0.64	0.86
6/14/96	190	6/11/96	ARB-09	48	0.46	0.20
6/14/96	191	6/11/96	J-9	49	2.52	1.78
6/14/96	192	6/11/96	S-9	50	0.37	0.60
6/14/96	193	6/11/96	K-9	51	0.92	1.38
6/14/96	194	6/11/96	UC-9	52	0.70	0.92
6/14/96	195	6/12/96	ARB-10	53	0.31	<0.20
6/14/96	196	6/12/96	ARB-10D	54	0.57	<0.20
6/14/96	197	6/12/96	J-10	55	3.29	1.10
6/14/96	198	6/12/96	J-10D	56	3.36	1.10
6/14/96	199	6/12/96	s-10	57	0.76	0.79
6/14/96	200	6/12/96	S-10D	58	0.83	0.77
6/14/96	201	6/12/96	K-10	59	1.61	1.12
6/14/96	202	6/12/96	K-10D	60	1.41	0.98
6/14/96	203	6/12/96	UC-10	61	0.89	0.68
6/14/96	204	6/12/96	UC-10D	62	0.74	0.74
6/14/96	205	6/13/96	ARB-11	63	0.46	<0.20
6/14/96	206	6/13/96	J-11	64	1.75	0.51
6/14/96	207	6/13/96	S-11	65	15.10	1.67
6/14/96	208	6/13/96	K-11	66	0.62	0.25
6/14/96	209	6/13/96	UC-11	67	0.45	0.45
6/14/96	210	6/13/96	UC-11B	68	<0.20	<0.20
6/20/96	219	6/16/96	ARB-12	69	<0.20	<0.20
6/20/96	221	6/16/96	K-12	71	1.48	0.54
6/20/96	222	6/16/96	S-12	72	0.47	0.27
6/20/96	223	6/16/96	J-12	73	0.39	<0.20
6/20/96	224	6/16/96	UC-12	74	<0.20	0.37
6/20/96	225	6/17/96	ARB-13	75	<0.20	<0.20
6/20/96	227	6/17/96	K-13	77	1.84	0.61
6/20/96	228	6/17/96	S-13	78	0.52	0.27
6/20/96	229	6/17/96	J-13	79	0.39	<0.20



### Appendix C. Ambient Site Individual Results for Chlorpyrifos and Chlorpyrifos Oxon (Cont.)

Trace Analytical Laboratory		Air Resources Board			Chlorpyrifos µg/Sample	Chlorpyrifos Oxon µg/Sample
Receiving Date	Sample I. D.	Sample Date	Sample I. D.	Log #		
6/20/96	230	6/17/96	UC-13	80	<0.20	0.33
6/20/96	231	6/18/96	ARB-14	81	0.20	<0.20
6/20/96	232	6/18/96	ARB-14D	82	0.46	0.34
6/20/96	234	6/18/96	K-14	84	1.10	0.68
6/20/96	235	6/18/96	S-14	85	0.69	0.36
6/20/96	236	6/18/96	J-14	86	1.07	0.46
6/20/96	237	6/18/96	UC-14	87	0.45	0.21
6/20/96	238	6/19/96	ARB-15	88	<0.20	0.24
6/20/96	241	6/19/96	K-15	91	0.69	0.81
6/20/96	242	6/19/96	K-15D	92	0.69	0.71
6/20/96	243	6/19/96	S-15	93	0.68	0.46
6/20/96	244	6/19/96	S-15D	94	0.72	0.45
6/20/96	245	6/19/96	J-15	95	0.80	0.72
6/20/96	246	6/19/96	J-15D	96	1.05	0.93
6/20/96	247	6/19/96	UC-15	97	<0.20	0.37
6/20/96	248	6/19/96	UC-15D	98	0.44	0.32
6/20/96	249	6/19/96	Blank	99	<0.20	<0.20
6/28/96	263	6/24/96	ARB-16	105	<0.20	<0.20
6/28/96	265	6/24/96	K-16	107	0.32	<0.20
6/28/96	266	6/24/96	S-16	108	<0.20	<0.20
6/28/96	267	6/24/96	J-16	109	0.32	<0.20
6/28/96	268	6/24/96	UC-16	110	0.23	<0.20
6/28/96	269	6/25/96	ARB-17	111	<0.20	<0.20
6/28/96	271	6/25/96	K-17	113	0.86	0.59
6/28/96	272	6/25/96	S-17	114	0.60	0.32
6/28/96	273	6/25/96	J-17	115	0.79	0.46
6/28/96	274	6/25/96	UC-17	116	0.30	0.23
6/28/96	275	6/26/96	ARB-18	117	<0.20	<0.20
6/28/96	276	6/26/96	ARB-18D	118	<0.20	<0.20
6/28/96	278	6/26/96	K-18	120	0.65	<0.20
6/28/96	279	6/26/96	K-18D	121	0.61	0.24
6/28/96	280	6/26/96	S-18	122	<0.20	<0.20
6/28/96	281	6/26/96	S-18D	123	<0.20	<0.20
6/28/96	282	6/26/96	J-18	124	0.74	0.22
6/28/96	283	6/26/96	J-18D	125	0.64	0.21
6/28/96	284	6/26/96	UC-18	126	<0.20	<0.20
6/28/96	285	6/26/96	UC-18D	127	<0.20	<0.20
7/2/96	286	6/27/96	ARB-19	128	<0.20	<0.20

### Appendix C. Ambient Site Individual Results for Chlorpyrifos and Chlorpyrifos Oxon (Cont.)

Trace Analytical Laboratory		Air Resources Board			Chlorpyrifos µg/Sample	Chlorpyrifos Oxon µg/Sample
Receiving Date	Sample I. D.	Sample Date	Sample I. D.	Log #		
7/2/96	288	6/27/96	K19	130	0.31	<0.20
7/2/96	289	6/27/96	S19	131	1.03	0.33
7/2/96	290	6/27/96	J19	132	1.02	0.49
7/2/96	291	6/27/96	UC-19	133	co. 20	co. 20
7/2/96	292	6/28/96	ARB-20	134	co. 20	0.21
7/2/96	294	6/28/96	K-20	136	0.69	0.70
7/2/96	295	6/28/96	s-20	137	0.48	0.32
7/2/96	296	6/28/96	J-20	138	0.65	0.50
7/2/96	297	6/28/96	UC-20	139	0.24	0.32
7/2/96	298	6/29/96	ARB-21	140	<0.20	<0.20
7/2/96	299	6/29/96	K-21	141	0.29	<0.20
7/2/96	300	6/29/96	S-21	142	<0.20	<0.20
7/2/96	301	6/29/96	J-21	143	0.28	0.20
7/2/96	302	6/29/96	UC-21	144	<0.20	0.29
7/2/96	303	6/29/96	Blank	145	<0.20	<0.20

## Appendix D. Application Site Results for Chlorpyrifos and Chlorpyrifos Oxon Results

ARB Log #	Type Sample Name	TAL Sample I. D.	Chlorpyrifos $\mu\text{g}/\text{sample}$	Chlorpyrifos Oxon $\mu\text{g}/\text{sample}$
Control	Resin	182C	<0.20	<0.20
1	E-1	143	11.7	0.59
3	S-1	144	15.3	0.81
5	N-1	145	5.21	0.20
6	S-2	146	125	6.93
7	E-2	147	42.4	3.34
8	E-2D	148	61.2	3.73
9	N-2	149	46.7	3.33
10	S-3	150	0.25	0.22
11	E-3	151	21.3	2.55
12	E-3D	152	68.5	4.37
13	N-3	153	15.7	2.44
14	N-4	154	0.93	2.33
15	S-4	155	1.94	2.69
16	E-4	156	10.4	6.98
17	E-4D	157	9.82	7.15
18	N-5	158	10.1	0.98
19	S-5	159	48.6	3.18
20	E-5	160	20.0	2.60
21	E-5D	161	38.5	3.15
22	N-6	162	207	11.2
23	S-6	163	34.5	4.92
24	E-6	164	33.4	4.89
25	E-6D	165	32.5	4.45
26	N-7	166	130	8.61
27	S-7	167	66.7	5.66
28	E-7	168	131	14.5
29	E-7D	169	138	14.9
31	N-8	170	93.4	18.3
32	S-8	171	59.4	8.48
33	E-8	172	102	16.9
34	E-8D	173	103	18.1
30	APP-B1	186	<0.20	<0.20

## **Appendix E. MSD Chromatograms for Confirmation of Chlorpyrifos and Chlorpyrifos Oxon**

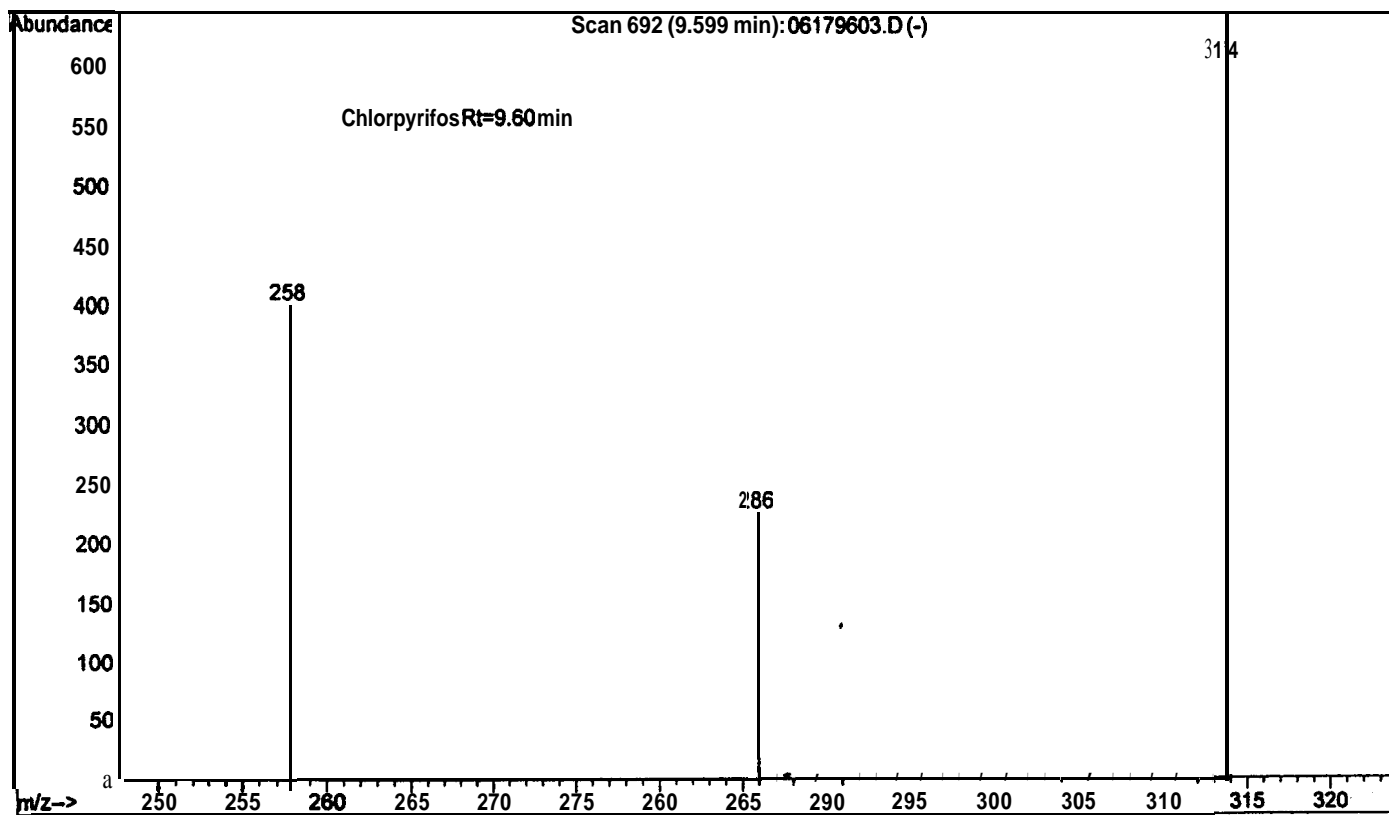
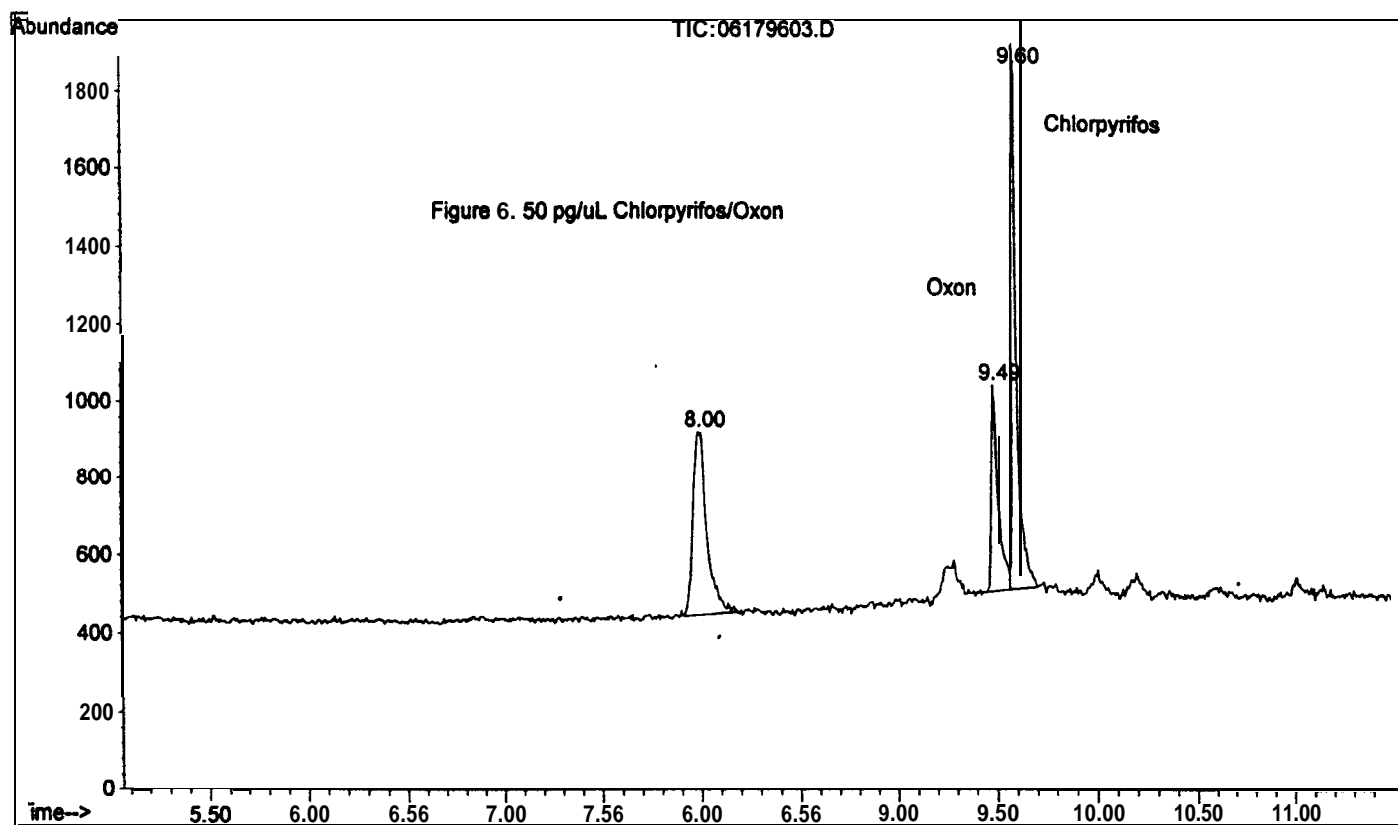
### **Chlorpyrifos Analysis**

- Figure 6. 50 pg/ $\mu$ L of Chlorpyrifos/Chlorpyrifos Oxon  
Figure 7. XAD-4 Resin Blank  
Figure 8. 2.5  $\mu$ g Chlorpyrifos/Chlorpyrifos Oxon Resin Fortification  
Figure 9. Ambient Site Air Sample

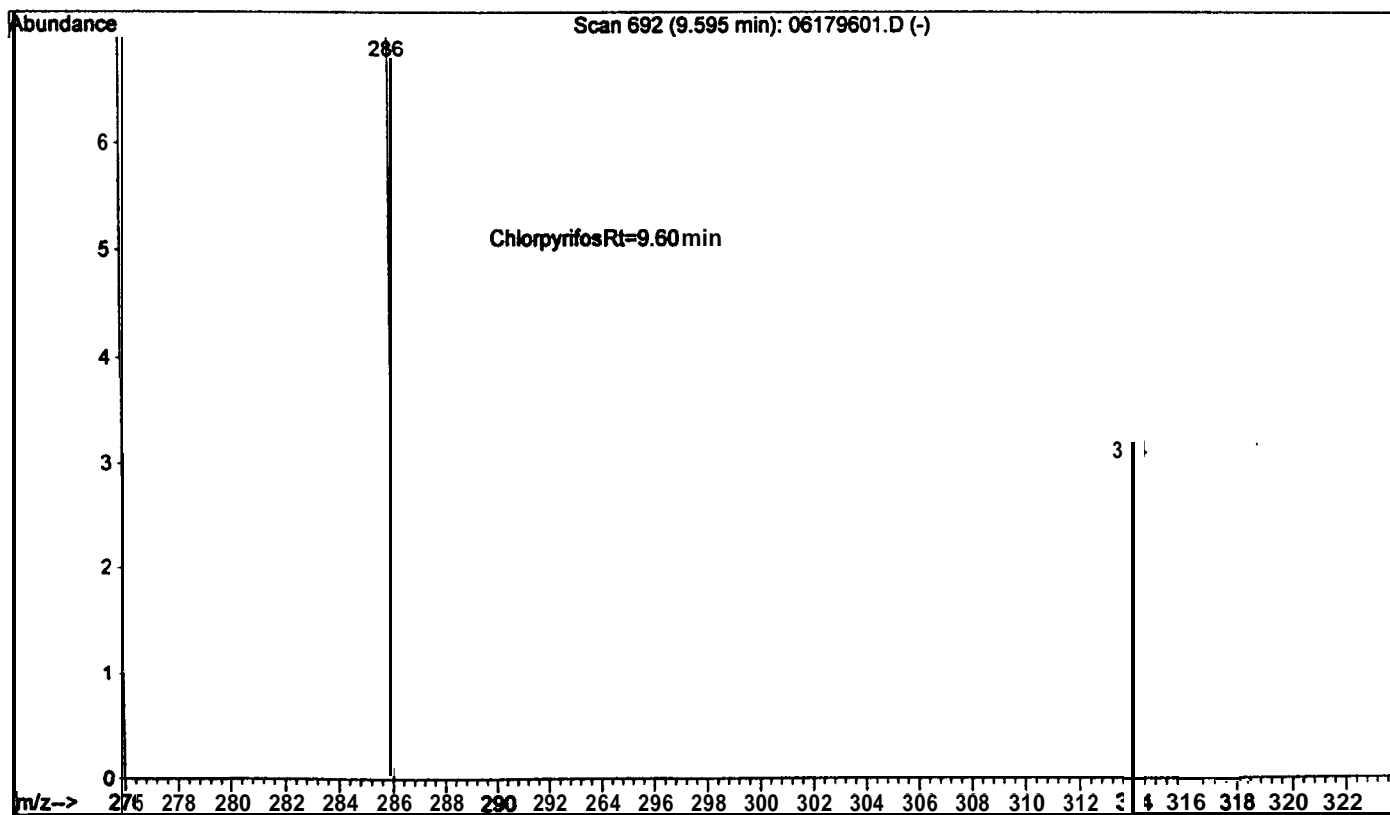
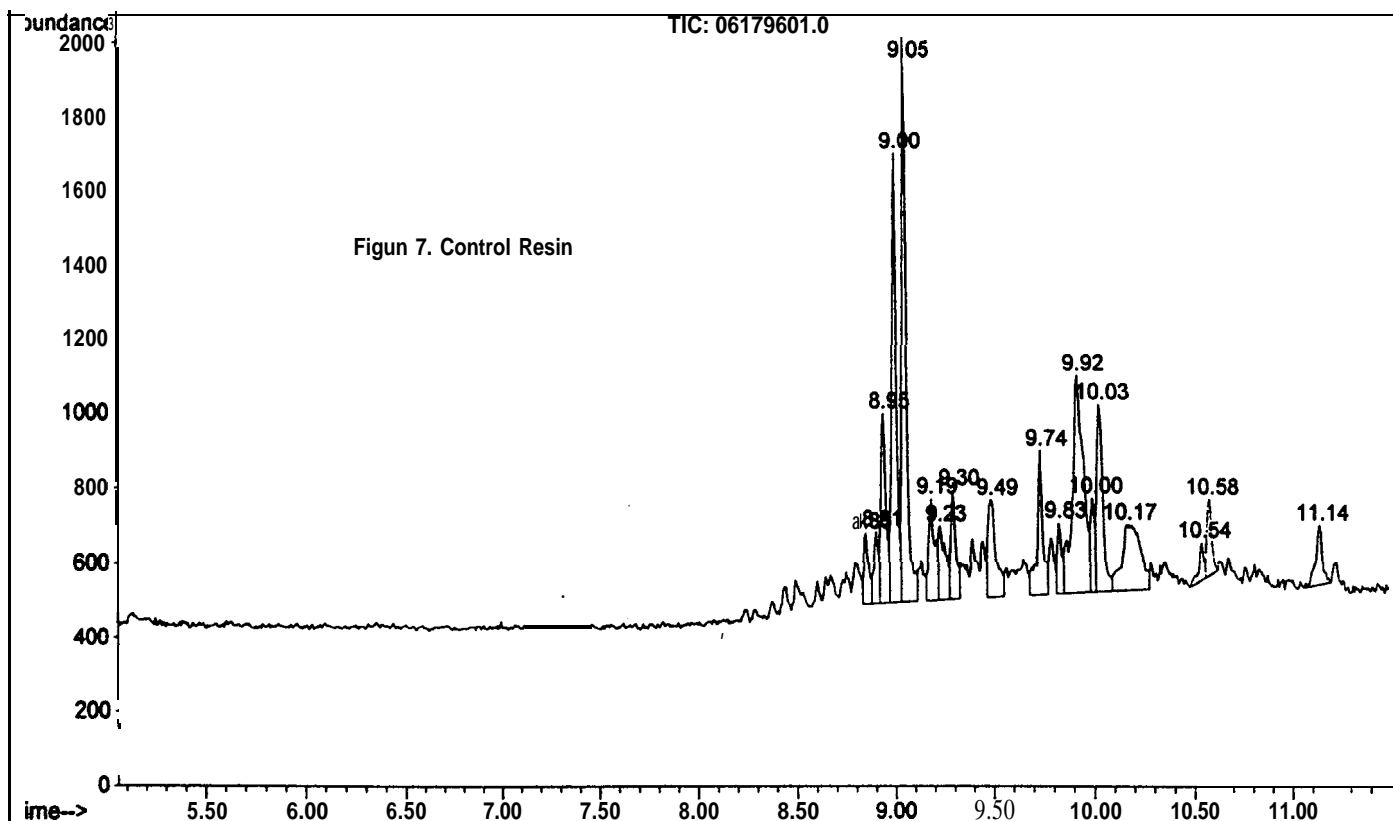
### **Chlorpyrifos Oxon Analysis**

- Figure 10. 25 pg/ $\mu$ L of Chlorpyrifos/Chlorpyrifos Oxon  
Figure 11. XAD-4 Resin Blank  
Figure 12. 2.5  $\mu$ g Chlorpyrifos/Chlorpyrifos Oxon Resin Fortification  
Figure 13. Ambient Site Air Sample

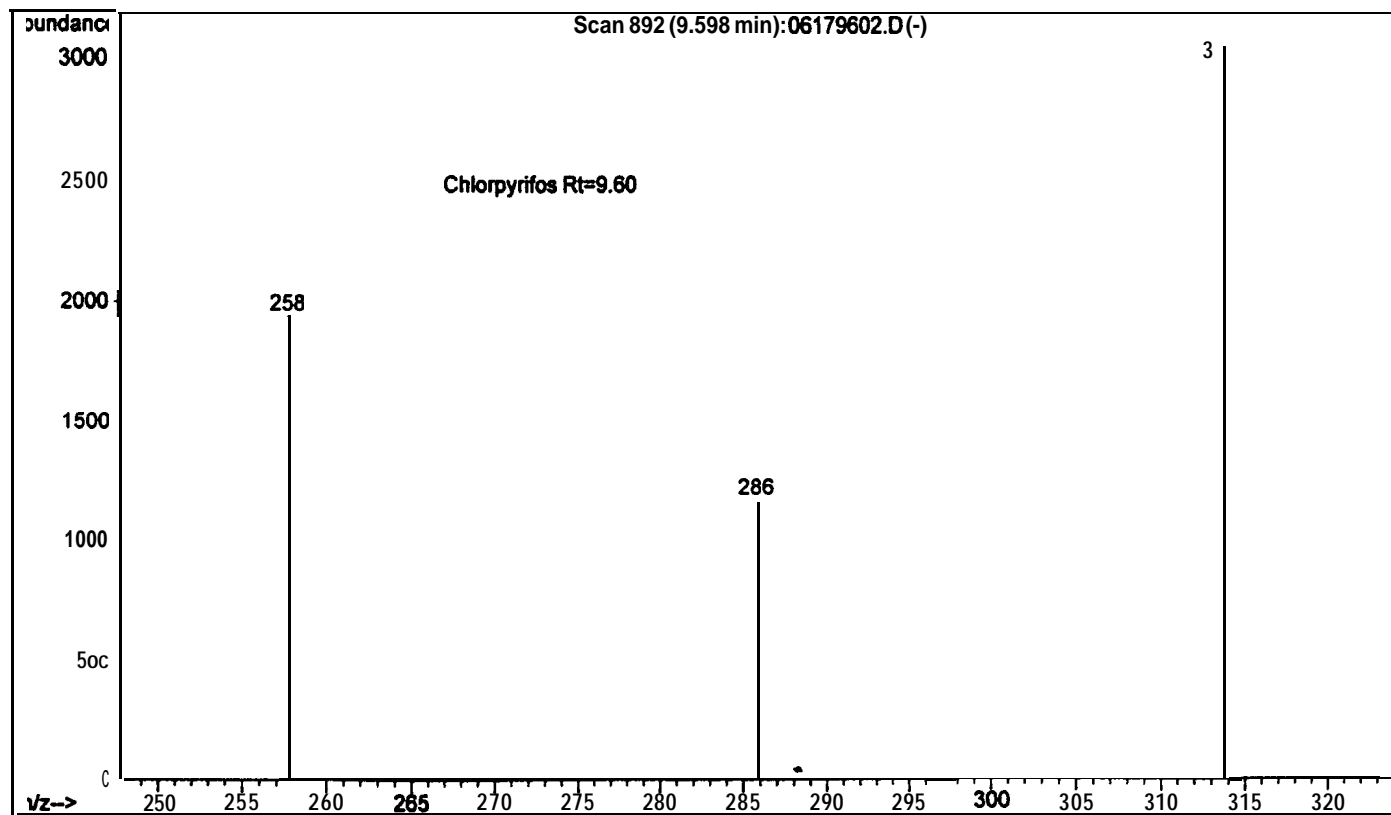
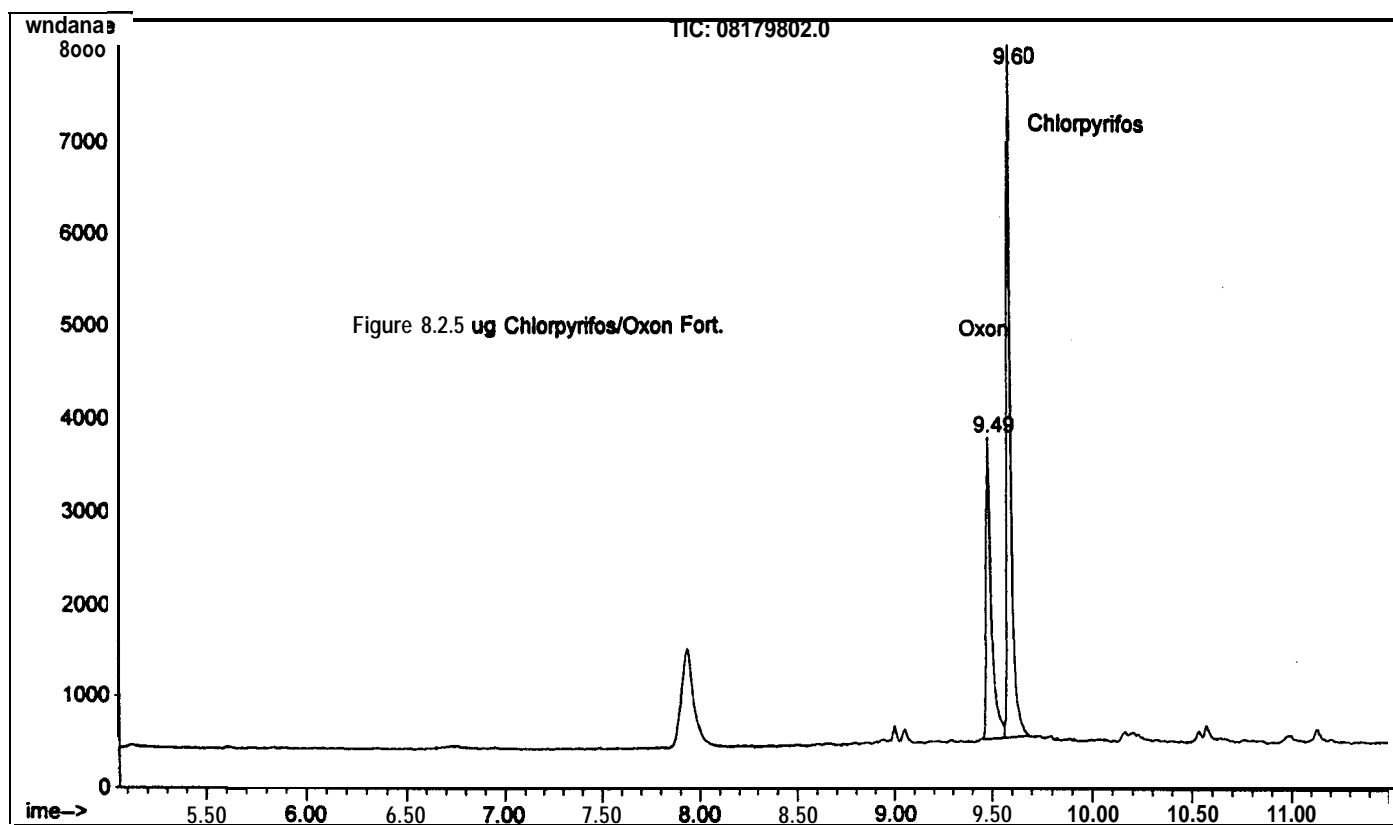
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Operator : Matt Hengel  
Acquired : 17 Jun 96 3:55 pm using AcqMethod CHLORPYR  
Instrument : GC/MS Ins  
Sample Name: 50 pg/ul 3ul inj.  
Misc Info :  
Vial Number: 3



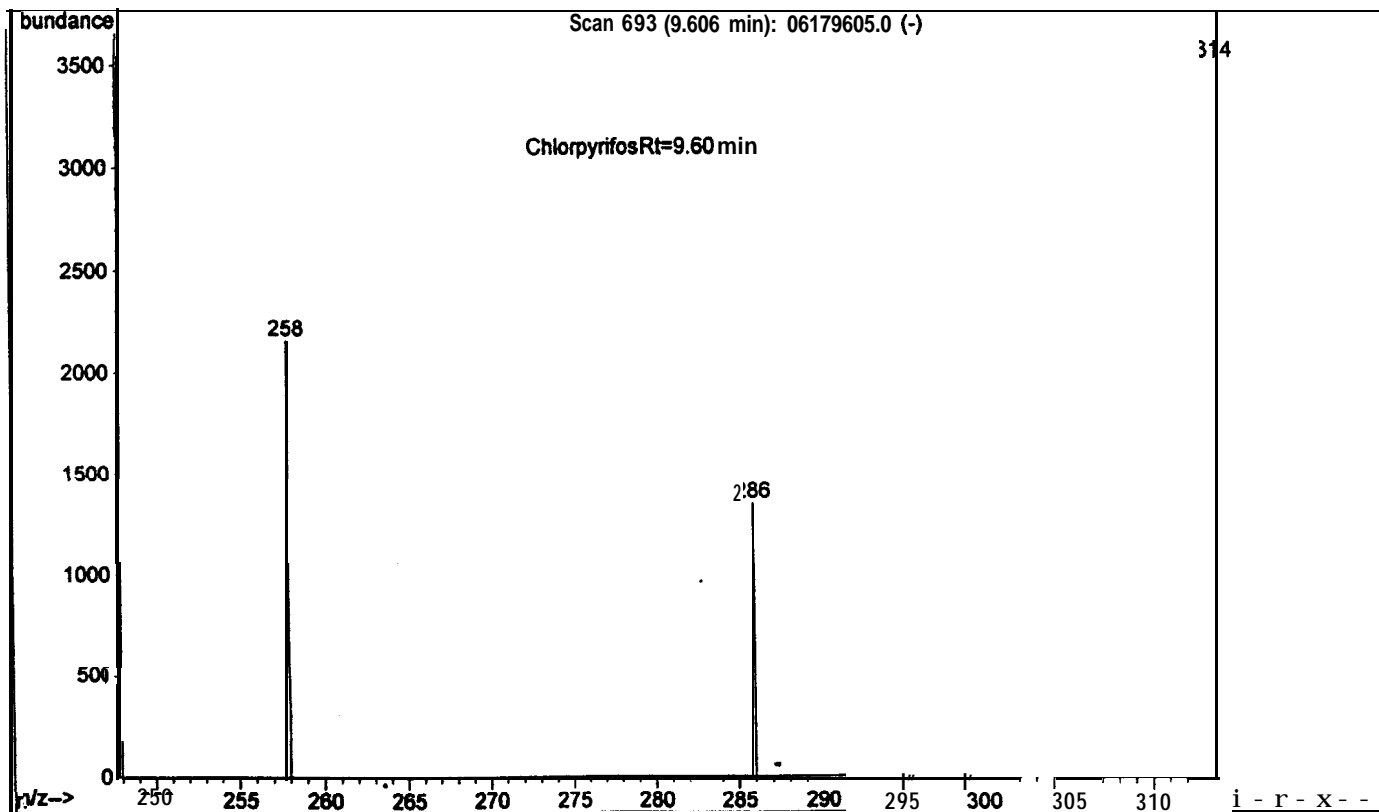
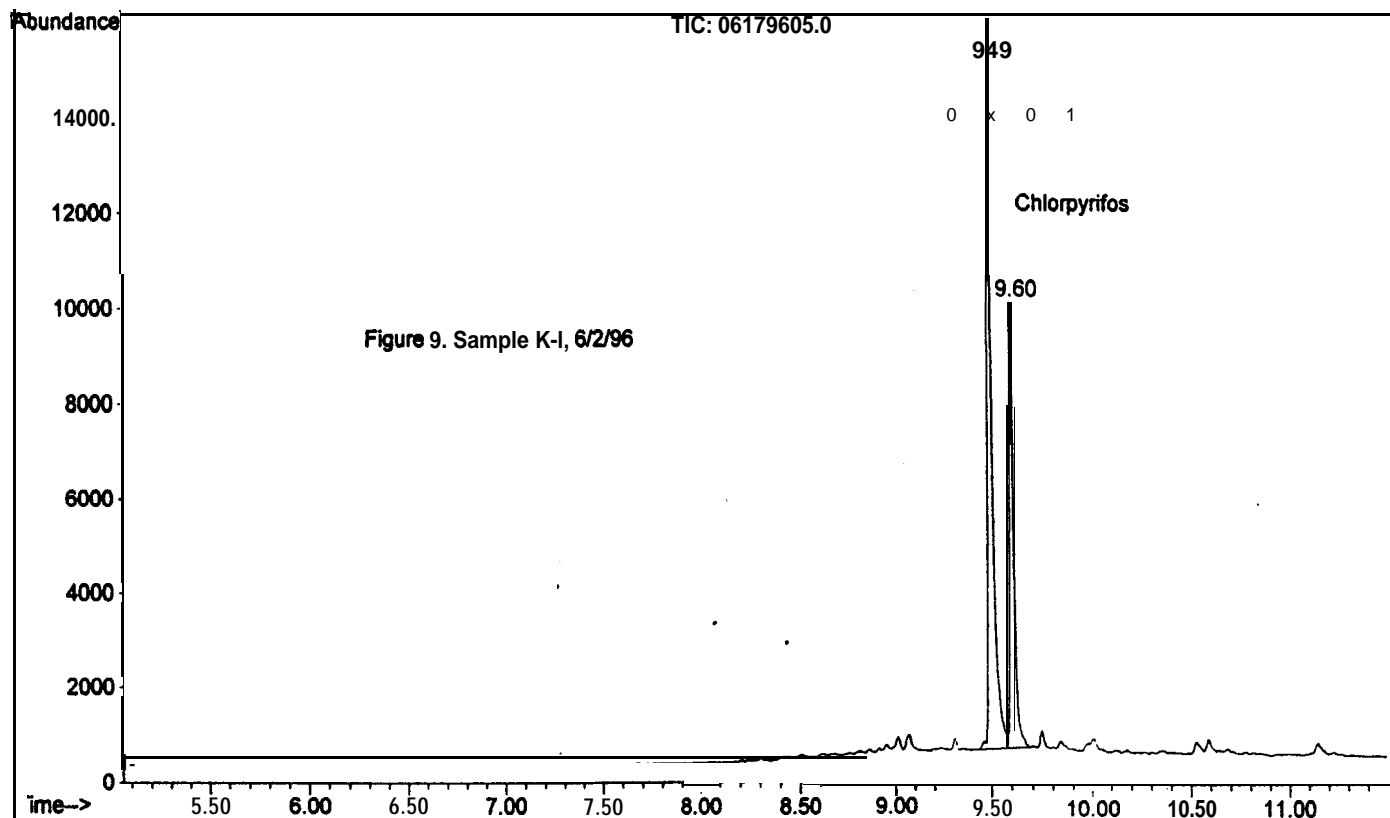
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Operator : Matt Hengel  
Acquired : 17 Jun 96 3:24 pm using AcqMethod CHLORPYR  
Instrument : GC/MS Ins  
Sample Name: 142 Blank Sample/4ml 3ul inj.  
Misc Info :  
Vial Number: 1



File : D:\MSDATA\TAL\ARB.96\CHLORPYR\06179602.D  
Operator : Matt Hengel  
Acquired : 17 Jun 96 3:40 pm using AcqMethod CHLORPYR  
Instrument : GC/MS Ins  
Sample Name: 212V2.5R4 Sample/10ml 3ul inj.  
Misc Info :  
Vial Number: 2

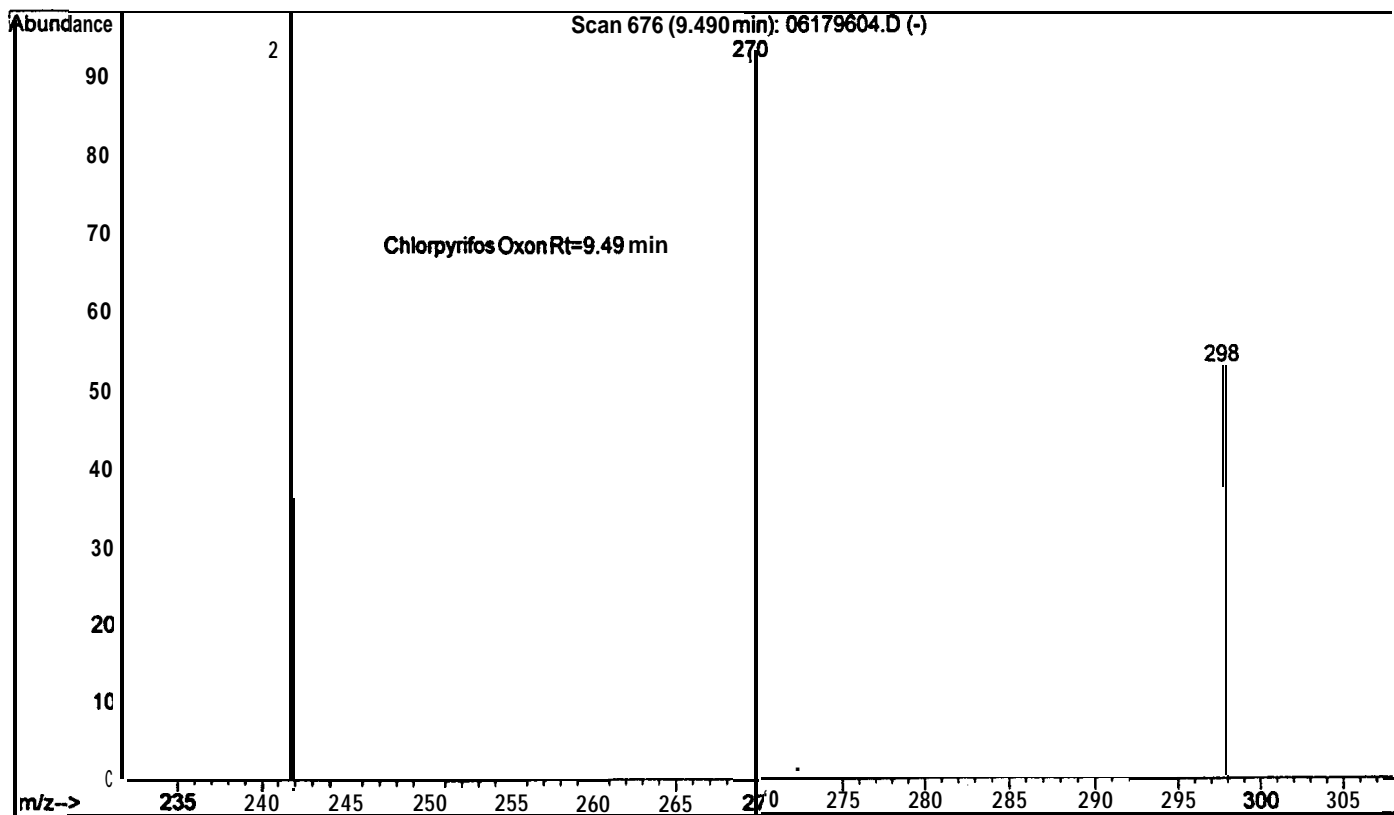
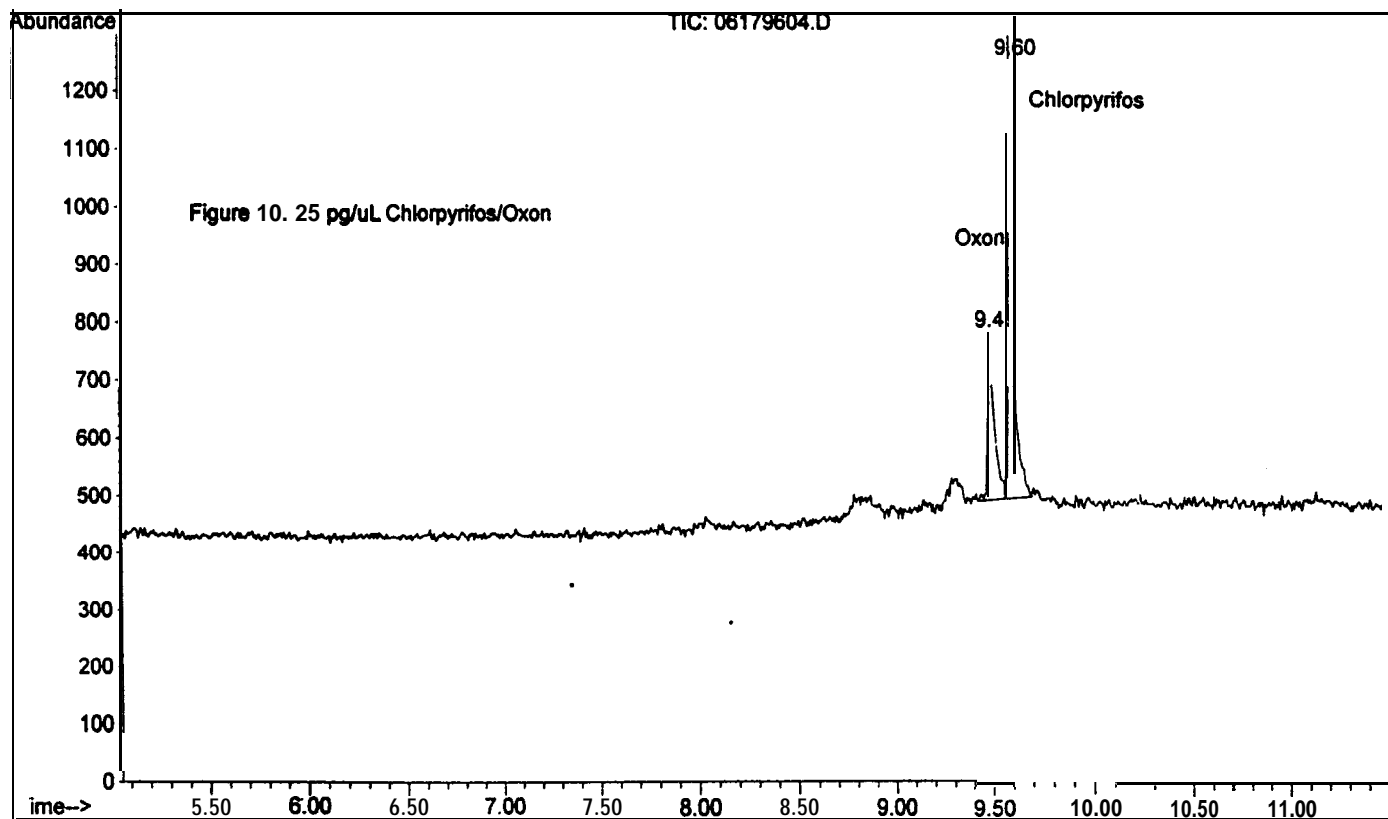


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Operator : Matt Hengel  
Acquired : 17 Jun 96 4:25 pm using AcqMethod CHLORPYR  
Instrument : GC/MS Ins  
Sample Name: 118 K-1 Sample/8ml 3ul inj.  
Misc Info :  
Vial Number: 5

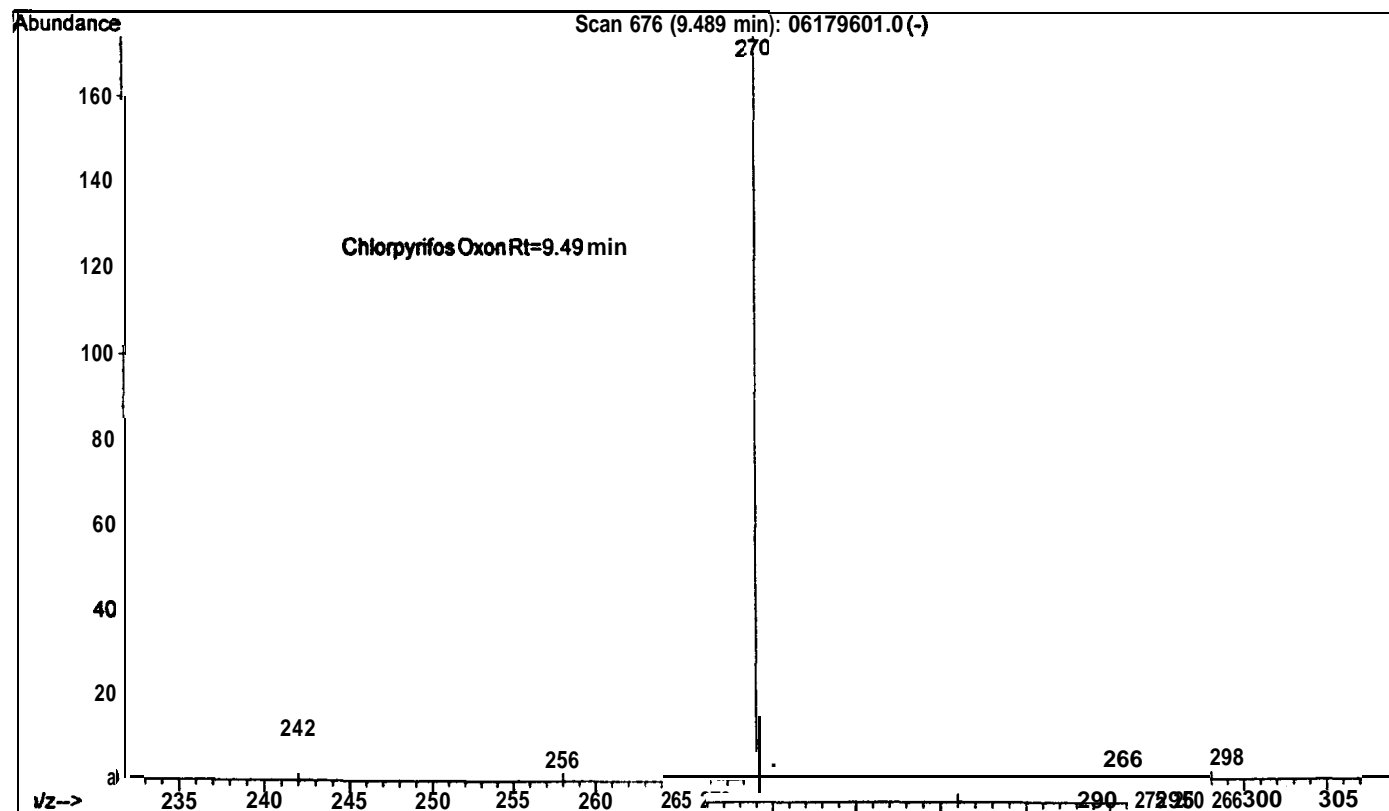
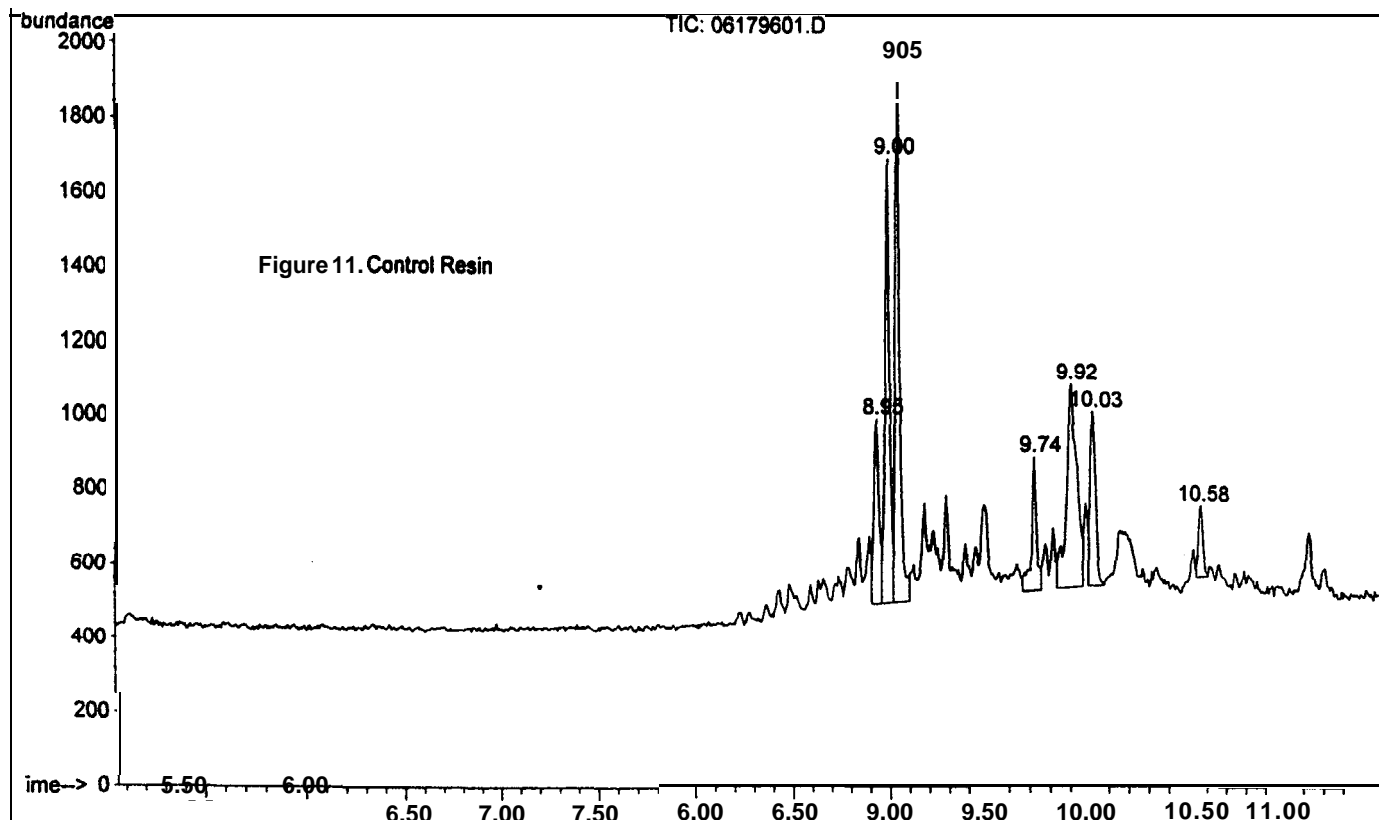




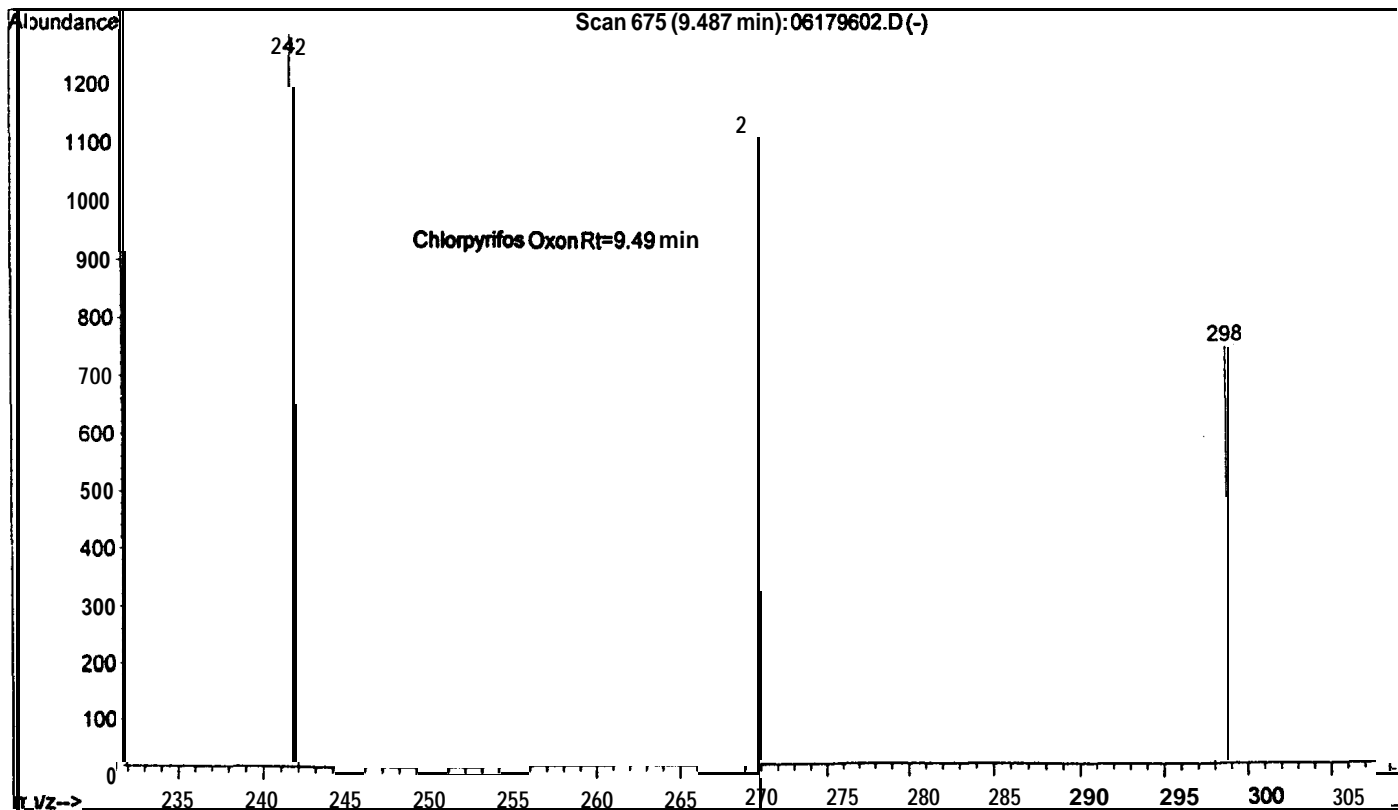
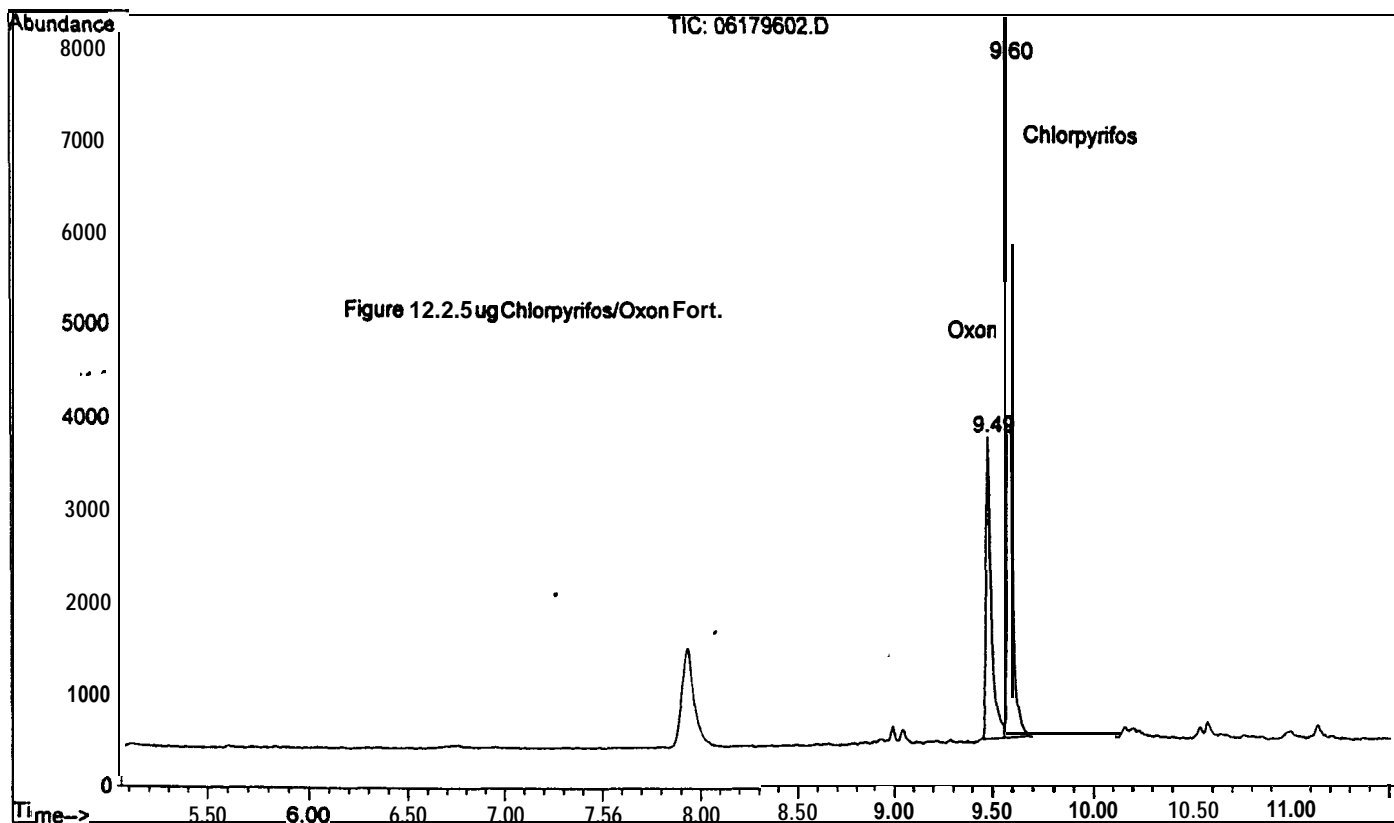
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Operator : Matt Hengel  
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Instrument : GC/MS Ins  
Sample Name: 25 pg/ul 3ul inj.  
Misc Info :  
Vial Number: 4



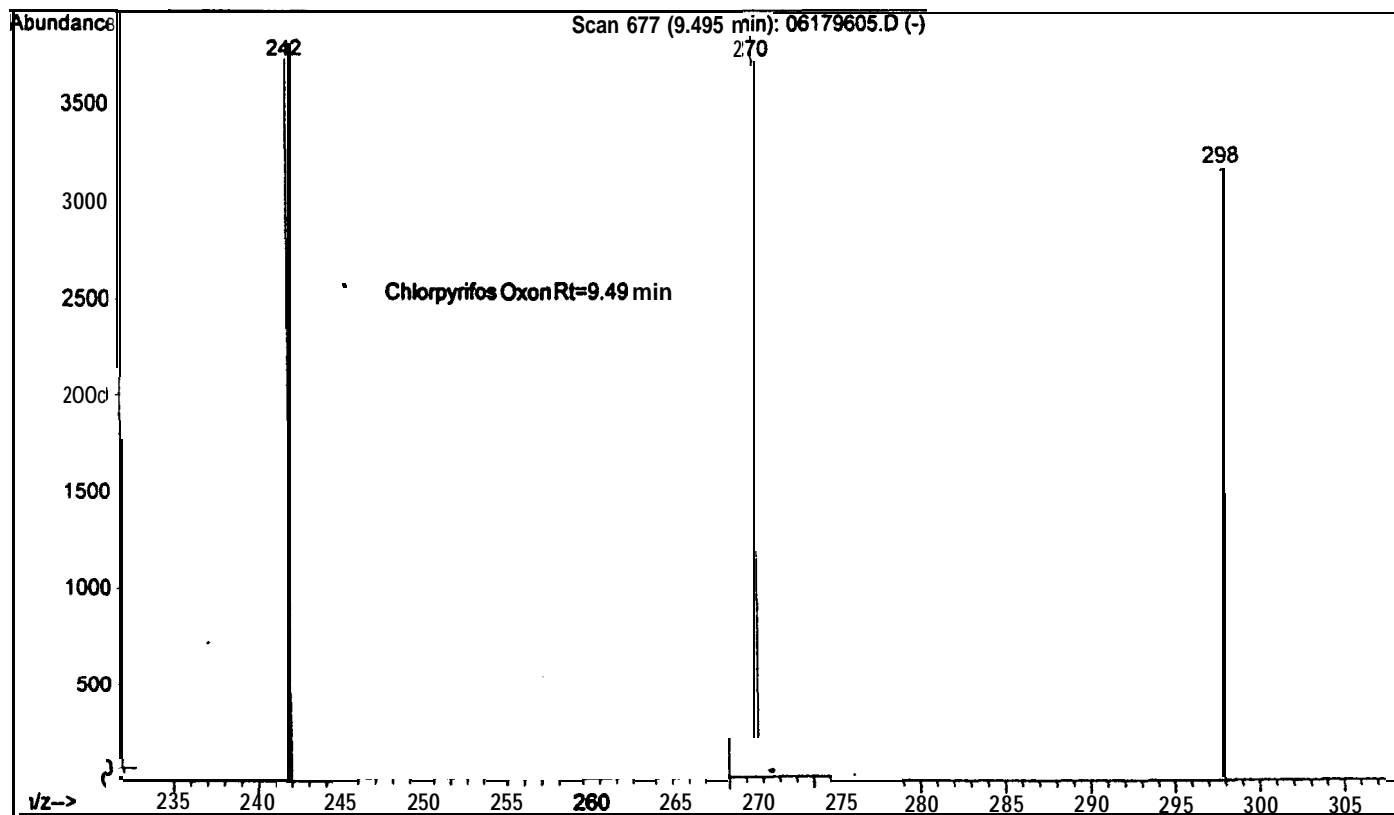
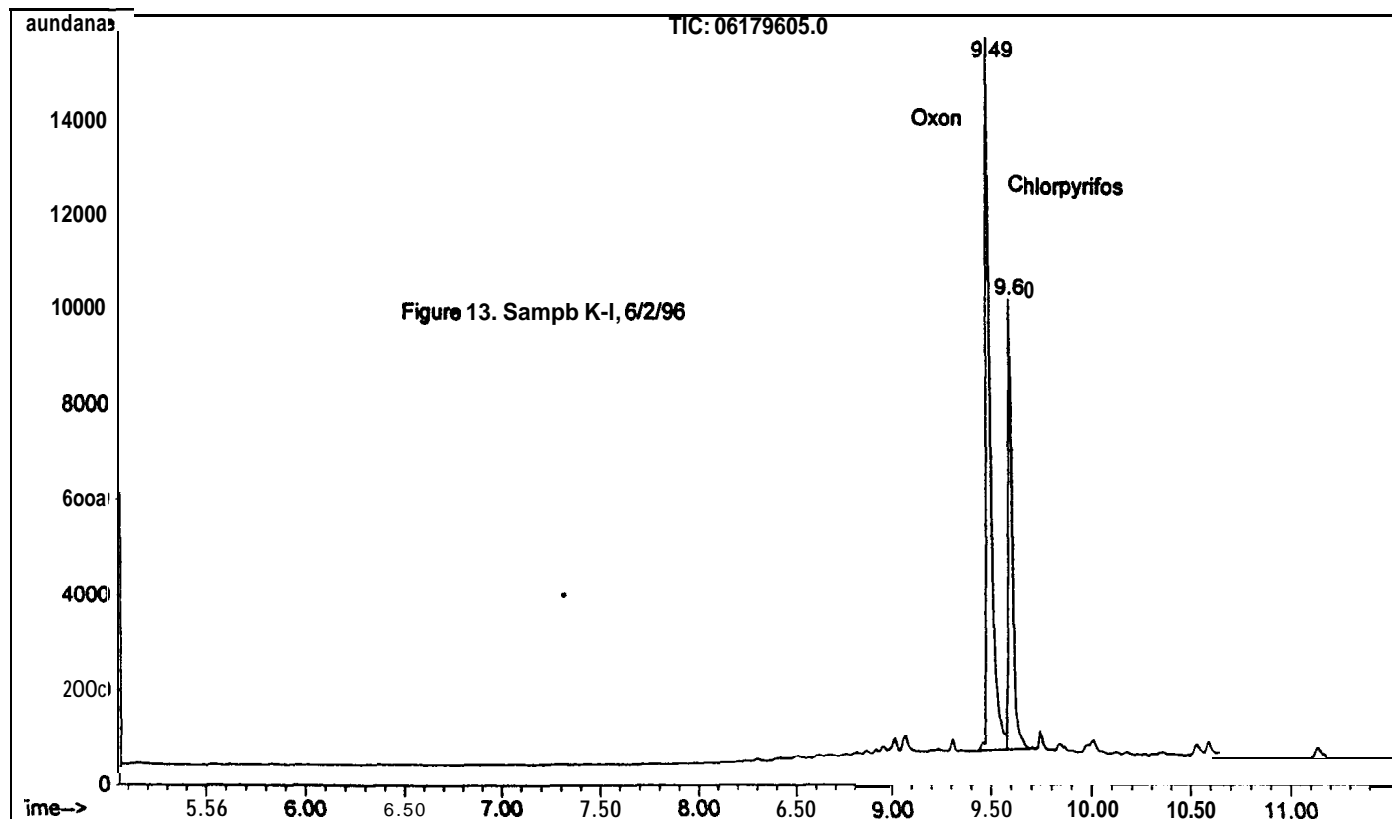
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Operator : Matt Hengel  
Acquired : 17 Jun 96 3:24 pm using AcqMethod CHLORPYR  
Instrument : GC/MS Ins  
Sample Name: 142 Blank Sample/4ml 3ul inj.  
Misc Info  
Vial Number: 1



File : D:\MSDATA\TAL\ARB.96\CHLORPYR\06179602.D  
Operator : Matt Hengel  
Acquired : i7 Jun 96 3:40 pm using AcqMethod CHLORPYR  
Instrument : GC/MS Ins  
Sample Name: 212V2.5R4 Sample/10ml 3ul inj.  
Misc Info :  
Vial Number: 2



File : D:\MSDATA\TAL\ARB.96\CHLORPYR\06179605.D  
Operator : Matt Hengel  
Acquired : 17 Jun 96 4:25 pm using AcqMethod CHLORPYR  
Instrument : GC/MS Ins  
Sample Name: 118 K-1 Sample/8ml 3ul inj.  
Misc Info :  
Vial Number: 5



## Appendix F. Qualitative MSD Confirmation Results

Sample ID	Sample Type	MSD Analysis Date	Chlorpyrifos	Chlorpyrifos Oxon
091C	Control Resin Sample	6/5/96	- <sup>1</sup>	-
088V0.2R1	0.20 µg Resin Fort	6/5/96	+ <sup>2</sup>	+
Standard	50 pg/µL	6/5/96	+	+
ARB-3	Ambient Air Sample	6/5/96	+	+
K-3	Ambient Air Sample	6/5/96	+	+
B-1	Resin Blank	6/6/96	-	-
089V0.2R2	0.20 µg Resin Fort	6/6/96	+	+
Standard	50 pg/µL	6/6/96	+	+
Standard	25 pg/µL	6/6/96	+	+
J-1	Ambient Air Sample	6/6/96	+	+
K-1	Ambient Air Sample	6/6/96	+	+
S-1	Ambient Air Sample	6/6/96	+	+
142	Resin Blank	6/17/96	-	-
212V2.5R4	2.5 µg Resin Fort	6/17/96	+	+
Standard	50 pg/µL	6/17/96	+	+
118 K-1	Ambient Air Sample	6/17/96	+	+
123 K-2	Ambient Air Sample	6/17/96	+	+
126 UC-2	Ambient Air Sample	6/17/96	+	+
138 J-4	Ambient Air Sample	6/17/96	+	+
152 E-3D	Ambient Air Sample	6/17/96	+	+
162 N-6	Application Site	6/17/96	+	+
188 J-8	Ambient Air Sample	6/17/96	+	+
197 J-10	Ambient Air Sample	6/17/96	+	+
201 K-10	Ambient Air Sample	6/17/96	+	+
207 S-11	Ambient Air Sample	6/17/96	+	+

## Appendix F. Qualitative MSD Confirmation Results (Cont.)

Sample ID	Sample Type	MSD Analysis Date	Chlorpyrifos	Chlorpyrifos Oxon
168 E-7	Application Site	6/22/96	+	+
171 S-8	Ambient Air Sample	6/22/96	+	+
Standard	25 pg/μL	6/22/96	+	+
221 K-12	Ambient Air Sample	6/22/96	+	+
227 K-13	Ambient Air Sample	6/22/96	+	+
242 K-15D	Ambient Air Sample	6/22/96	+	+
247 UC- 15	Ambient Air Sample	6/22/96	+	+
271 K-17	Ambient Air Sample	7/2/96	+	+
273 J-17	Ambient Air Sample	7/2/96	+	+
278 K-18	Ambient Air Sample	7/2/96	+	+
282 J-18	Ambient Air Sample	7/2/96	+	+
Standard	50 pg/μL	7/2/96	+	+
289 S-19	Ambient Air Sample	7/2/96	+	+
290 J-19	Ambient Air Sample	7/2/96	+	+
294 K-20	Ambient Air Sample	7/2/96	+	+
296 J-20	Ambient Air Sample	7/2/96	+	+
225 ARB-13	Ambient Air Sample	7/16/96	+	+
228 S-13	Ambient Air Sample	7/16/96	+	+
234 K-14	Ambient Air Sample	7/16/96	+	+
243 s-15	Ambient Air Sample	7/16/96	+	+
Standard	50 pg/μL	7/16/96	+	+
268 UC-16	Ambient Air Sample	7/16/96	†	†
272 S-17	Ambient Air Sample	7/16/96	+	+
291 UC-19	Ambient Air Sample	7/16/96	+	+
292 ARB-20	Ambient Air Sample	7/16/96	+	+

**Appendix F. Qualitative MSD Confirmation Results (Cont.)**

Sample ID	Sample Type	MSD Analysis Date	Chlorpyrifos	Chlorpyrifos Oxon
297 UC-20	Ambient Air Sample	7/16/96	+	+
300s-21	Ambient Air Sample	7/16/96	+	+
302 UC-21	Ambient Air Sample	7/16/96	+	+

1. No residue detected at the 25 **pg/μL** level.
2. Residue detected above the 25 **pg/μL level**.

## **Appendix G. Standard Operating Procedures for Analysis of Chlorpyrifos and Chlorpyrifos Oxon in Ambient Air.**

### **1. SCOPE**

The method utilized is a gas chromatographic method with a flame photometric detector (FPD) and a 526 run filter that is selective for phosphorus compounds. This method has been used by Environmental Toxicology personnel for the analysis of organophosphates in air.

### **2. SUMMARY OF METHOD**

Exposed **XAD-4®** resin samples are stored either in an ice chest with dry ice or at -20 °C in a **freezer**. Samples are extracted with 75 mL ethyl acetate and an **aliquot** is concentrated prior to injecting 3 µL on to a gas **chromatograph** equipped with a flame photometric detector.

### **3. INTERFERENCES/LIMITATIONS**

Potential interferences may arise due to contaminants in laboratory solvents, reagents, glassware and/or apparatus. A reagent blank must be run through the method procedure and analyzed with each set of samples.

### **4. EQUIPMENT AND CONDITIONS**

#### **A. Instrumentation**

Hewlett-Packard 5890 Series II Gas Chromatograph  
Hewlett-Packard GC System Injector-Autosampler  
**Perkin-Elmer TurboChrom®** Data System, v. 4.1  
Microsoft Excel®, v. 7.0

Injector : 250 °C

Detector: 225 °C

Column: **Rxt-1** 30 m x 0.53 mm wide bore capillary with a 1.5 µm **film** thickness

Temperature program: initial: 180 °C, hold 1 min, ramp to 220 °C @ 10 °C/min; hold 1 min. Retention time : chlorpyrifos **oxon** = 4.68 min. ; chlorpyrifos = 4.87 min. Both chlorpyrifos and chlorpyrifos **oxon** are analyzed during the same chromatographic run.



Flows:

Carrier (He) = 20 mL/min

Make-up (He) = 10 mL/min

Air = 115 mL/min

Hydrogen = 100 mL/min

#### B. Auxiliary Apparatus

1. Rotary platform shaker
2. 100 mL round bottom flasks
3. 50 mL graduated cylinders
4. Rotary evaporator
5. Disposable pipettes
6. Nitrogen evaporator (N-Evap®)
7. Graduated 15 mL centrifuge tubes
8. Autosampler vials and screw caps

#### C. Reagents

1. Ethyl acetate, pesticide grade
2. Chlorpyrifos, Dow Elanco 99% or equivalent
- 3. Chlorpyrifos **oxon**, Dow Elanco 95% or equivalent

### 5. ANALYSIS OF SAMPLES

1. A solvent blank will be analyzed with each set of samples. The blank must be free of interferences for the analysis of both **chlorpyrifos** and chlorpyrifos **oxon**.
2. Three resin fortification samples must be fortified, extracted and analyzed with each set of samples.
3. Allow samples to come to room temperature and add 75 mL of ethyl acetate. Cap the sample and swirl for one hour on a rotary platform shaker.
4. Quantitatively transfer 37.5 mL to a 100 mL round bottom flask and evaporate the solvent to near dryness using a rotary evaporator.
5. Transfer sample using small aliquots of ethyl acetate to a graduated centrifuge tube. Adjust sample to an appropriate volume for injection on to the GC-FPD.

6. Transfer an aliquot of the adjusted sample to an Autosampler vial.
7. Inject 3  $\mu\text{L}$  of sample, along with the appropriate standard concentrations for chlorpyrifos and chlorpyrifos **oxon**, into the gas **chromatograph**. If the peak area for either the parent or the **oxon**, is larger than the highest standard, dilute the sample with ethyl acetate and re-inject.
8. Calculate the mass in  $\mu\text{g}$  based on the linear regression curve for **TurboChrom®** and the appropriate dilution factors.  
 Concentration ( $\mu\text{g/mL}$ ) x Dilution Factor (n&)/Sample =  $\mu\text{g/sample}$ .

## 6. QUALITY ASSURANCE

### A. Instrument Reproducibility

Triplicate injections of three standards at five different concentrations were made to establish the reproducibility of the instrument. The data for chlorpyrifos is given in Table 1.

Table 1. Instrument Reproducibility for Chlorpyrifos

<b>Chlorpyrifos injected (pg/<math>\mu\text{L}</math>)</b>	<b>Integration Counts</b>	<b>Percent (%)</b>
25	10682 $\pm$ 314	$\pm$ 2.94
50	20852 $\pm$ 961	$\pm$ 4.60
100	41856 $\pm$ 1247	$\pm$ 2.98
200	88037 $\pm$ 822	$\pm$ 0.93
400	166594 $\pm$ 9457	$\pm$ 5.68

Table 2. Instrument Reproducibility for **Chlorpyrifos Oxon**

<b>Chlorpyrifos Oxon injected (pg/<math>\mu\text{L}</math>)</b>	<b>Integration Counts</b>	<b>Percent (%)</b>
25	8503 $\pm$ 826	$\pm$ 9.71
50	17831 $\pm$ 1487	$\pm$ 8.34
100	35611 $\pm$ 4134	$\pm$ 11.6
200	73796 $\pm$ 6627	$\pm$ 8.98
400	143990 $\pm$ 19886	$\pm$ 13.8

## B. Linearity

A **five** point calibration curve of chlorpyrifos and chlorpyrifos **oxon**, with concentrations ranging **from** 0.025 µg/mL to 0.40 µg/mL, was injected 5 times during the course of a run that included a total of 72 injection. The run included XAD resin samples and fortified resin samples. The corresponding equations and correlation coefficients are:

For chlorpyrifos:

$$Y = 420.616 *x + 296.404 \quad \text{Corr}(r^2) = 0.9966$$

For chlorpyrifos **oxon**:

$$Y = 368.0479*x - 27.656 \quad \text{Corr}(r^2) = 0.9834$$

## C. Minimum Detection Limit

The minimum detection limit (mdl) is set by the minimum concentration injected (25 pg/µL) times the minimum total volume (2.0 mL) times the dilution factor (one-half of the sample used). The minimum detectable is 0.10 µg/sample.

Assuming a total air sampling rate of 15 lpm for 24 hours, the total air volume processed would be: 21 m<sup>3</sup> and the air concentration = 0.10 µg/21 m<sup>3</sup> = 4.6 ng/m<sup>3</sup>

## D. Laboratory Recovery Data and Air Collection Efficiency (air trapping) of Chlorpyrifos and Chlorpyrifos oxon

Laboratory recovery data for chlorpyrifos and chlorpyrifos **oxon** is given in Table 3 and 4 while air collection data for chlorpyrifos run on March **23, 1996** is given in Table 5. A second set of air collection data for chlorpyrifos is given in Table 6. The air collection data for chlorpyrifos **oxon** is given in Table 7.

The major difference between Tables 5 and 6 is that the ambient temperature was different for the corresponding experiment. It should be noted that glass wool is used **only** for trapping experiments and not during ambient or application site sampling. From the data in Tables 5 and 6, as well as previous experimentation, it appears that glass wool is a prime cause of the conversion of a thioorganophosphate to its corresponding **oxon**.

Table 3. Laboratory Recovery of Chlorpyrifos from Resin Spikes

Sample	Fortification ( $\mu\text{g}$ )	Recovery ( $\mu\text{g}$ )	% Rec	Average	Stdev.
014V50R1	50	48.97	98%		
015V50R2	50	49.56	99%		
016V50R3	50	50.04	100%		
017V50R4	50	49.85	100%		
036V0.2R1	0.20	0.19	95%		
037V0.2R2	0.20	0.21	105%		
038V0.2R3	0.20	0.21	105%		
039V0.2R4	0.20	0.18	90%	99%	7%

Table 4. Laboratory Recovery of Chlorpyrifos/Oxon from Resin Spikes

Sample	Parent			Oxon					
	Fortification ( $\mu\text{g}$ )	Recovery ( $\mu\text{g}$ )	% Rec	Parent Average	Parent Stdev.	Recovery ( $\mu\text{g}$ )	Oxon % Rec	Oxon Average	Oxon Stdev.
082V50R1	50	51.70	103%			50.56	101%		
083V50R2	50	50.86	102%			52.60	105%		
084V50R3	50	51.43	103%			52.45	105%		
088V0.2R1	0.2	0.21	106%			0.23	114%		
089V0.2R2	0.2	0.21	107%			0.23	117%		
090V0.2R3	0.2	0.19	94%	103%	5%	0.21	103%	108%	6%

Table 5. Chlorpyrifos Air Collection Experiments Run on March 23, 1996<sup>A, B, C</sup>

Sample	Glass Wool	Primary	Trapping Efficiency	Total Mass Recovery	Oxonin Primary	Oxon as Parent	Sum of P + O	Trapping Efficiency
50 ( $\mu\text{g}$ )	( $\mu\text{g}$ )	( $\mu\text{g}$ )	(%)	(%)	( $\mu\text{g}$ )	( $\mu\text{g}$ )	( $\mu\text{g}$ )	(%)
Trap Eff. Rep. 1	0.49	40.04	81	81	6.47	6.78	46.82	94
Trap Eff. Rep. 2	0.16	37.10	74	75	7.08	7.42	44.52	89
Trap Eff. Rep. 3	0.25	42.57	86	86	6.18	6.48	49.05	98
Trap Eff. Rep. 4	0.43	42.67	86	86	6.40	6.71	49.38	99

A: Samplers ran for 24 hours @ ~ 25 Lpm; Maximum temperature 20 °C

B: No chlorpyrifos or chlorpyrifos oxon was found in the back up trap

C: No chlorpyrifos oxon was found on the glass wool samples

"Oxon as Parent" is a molar conversion of the oxon to the parent compound.

"Sum of P + O" is the sum of the converted oxon and the parent found.

"Total Mass Recovery" is = [(Glass wool ( $\mu\text{g}$ ) + Primary ( $\mu\text{g}$ )) x 100]/amt. spiked ( $\mu\text{g}$ ).

"Trapping Efficiency" is = (Primary ( $\mu\text{g}$ ) x 100)/(amt. spiked ( $\mu\text{g}$ ) - amt. recovered on Glass wool).

Table 6. Chlorpyrifos Air Collection Experiments Run on April 30, 1996<sup>A,B,C</sup>

Sample 50 (µg)	Glass Wool (µg)	Primary (µg)	Trapping Efficiency (%)	Total Mass Recovery (%)	Oxon in Primary (µg)	Oxon as Parent (µg)	Sum of P + O (µg)	Trapping Efficiency (%)
Trap Eff. Rep. 1	<0.10	17.38	35	35	19.32	20.25	37.63	75
Trap Eff. Rep. 2	<0.10	17.55	35	35	22.06	23.12	40.67	81
Trap Eff. Rep. 3	<0.10	17.93	36	36	20.58	21.57	39.50	79
Trap Eff. Rep. 4	<0.10	20.38	41	41	19.71	20.65	41.03	82

A: Samplers ran for 24 hours @ ~ 25 Lpm; Maximum temperature 35 °C

B: No chlorpyrifos or chlorpyrifos oxon was found in the back up trap

C: No chlorpyrifos oxon was found on the glass wool samples

Table 7. Chlorpyrifos Oxon Air Collection Experiments Run on April 30, 1996<sup>A,B, C</sup>

Sample 50 (ug)	Glass Wool (µg)	Primary (µg)	Trapping Efficiency (%)	Total Mass Recovery (%)
Trap Eff. Rep. 1	<0.10	41.10	82	82
Trap Eff. Rep. 2	<0.10	40.14	80	80
Trap Eff. Rep. 3	0.1	32.98	66	66
Trap Eff. Rep. 4	<0.10	34.52	69	69

A: Samplers ran for 24 hours @ ~ 25 Lpm; Maximum temperature 35 °C

B: No chlorpyrifos or chlorpyrifos oxon was found in the back up trap

C: No chlorpyrifos was found on the glass wool samples

#### E. Storage Stability

Table 8. Chlorpyrifos Storage Stability Samples\*

Sample	Fortification (µg)	Recovery (µg)	% Rec	Average	Stdev.
002S50R1	50	46.13	92%		
003S50R2	50	44.29	89%		
004S50R3	50	46.27	93%		
005S50R4	50	48.19	96%		
006S50R5	50	44.38	89%	92%	3%

A: 3/24/96-4/30/96, 37 Days of Storage in -20°C Freezer.

Table 9. Chlorpyrifos Oxon Storage Stability Samples<sup>A</sup>

Sample	Fortification (µg)	Recovery (µg)	% Rec	Average	Stdev.
041S50R11	50	50.45	101%		
042S50R12	50	49.41	99%		
043S50R13	50	50.45	101%		
044S50R14	50	50.72	101%		
045S50R15	50	50.16	100%	100%	1%

A: 4/30/96-5/31/96, 31 Days of Storage in -20°C Freezer.

## **Appendix H. Blank Resin Contamination.**

During the analysis of 6/14/96 and 6/21/96 ambient samples, it was noticed that the laboratory resin blanks had residues of chlorpyrifos. The amount of chlorpyrifos found for 6/14/96 and 6/21/96 resin blanks were 0.54 and 1.94  $\mu\text{g}$ , respectively. The source of the contamination was traced to a hood where the air sampling cartridges were filled with resin. Prior to the 6/14/96 analysis, on 6/11/96, fifteen **chlorpyrifos/chlorpyrifos oxon** quality assurance samples had been prepared using this hood. This procedure may have been the source of the contamination. The following steps were taken to prevent contamination to ambient resin samples.

The filled cartridges sent out for the next weeks ambient air sampling were recalled and sample cartridges were filled with new resin **from** a different lot (jar). As the result of the hood/resin contamination, the area for loading cartridges with resin was moved to a different location and a new lot of resin was used. This lot of resin was checked for residues of chlorpyrifos prior to use for the project.

This contamination does not fully explain the irregular quality assurance results for samples fortified with **chlorpyrifos/chlorpyrifos oxon** analog on 6/11/96. All quality assurance sample fortified with **chlorpyrifos/chlorpyrifos oxon** analog (4 application and 10 laboratory fortification samples) and concurrent validation (30 samples) run prior to, and subsequent to this set of quality assurance samples, were well within the acceptable recovery range.

There was no negative affects on the ambient and application sampling parts of the project. All field resin blank samples were below the limit of detection for chlorpyrifos. Furthermore, the background site did not have abnormal residues of chlorpyrifos detected.

## APPENDIX III

# QMOSB AUDIT REPORT





**Cal/EPA**

California  
Environmental  
Protection  
Agency



**Air Resources Board**

P.O. Box 2815  
2020 L street  
Sacramento, CA  
95812-2815

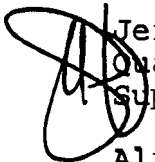



Pete Wilson  
Governor

James M. Strock  
Secretary for  
Environmental  
Protection

**MEMORANDUM**

TO: George Lew, Chief  
Engineering and Laboratory Branch

THROUGH:  Jeff Cook, Chief  
Quality Management and Operations  
Support Branch

FROM: Alice Westerinen, Manager   
Quality Assurance Section

DATE: May 28, 1997

SUBJECT: CHLORPYRIFOS QA SYSTEM AUDIT REPORT

---

Since there were no comments on the final draft system audit report dated April 18, 1997, please consider that report to be the final system audit report.

Thank you for participating in this audit. If you have any questions, please contact Mr. Russell Grace at (916) 322-7317.

Attachment

cc: Cindy Castronovo  
Kevin Mongar ✓  
Russell Grace

rdg/T10N15IU

STATE OF CALIFORNIA AIR RESOURCES BOARD  
MONITORING AND LABORATORY DIVISION  
QUALITY ASSURANCE SECTION

SYSTEM AUDIT REPORT  
APPLICATION AND AMBIENT AIR MONITORING  
OF CHLORPYRIFOS  
IN  
TULARE COUNTY

**FINAL DRAFT**

APRIL 1997

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CHLORPYRIFOS MONITORING  
IN  
**TULARE** COUNTY

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**ATTACHMENTS**

1. Air Sampler Used in the Monitoring of Chlorpyrifos
2. Flow Rate Audit Procedures for Air Samplers Used in Pesticide Monitoring
3. Performance Audit Procedures for the Laboratory Analysis of Chlorpyrifos and Chlorpyrifos **Oxon**

## I. EXECUTIVE SUMMARY

At the request of the California Department of Pesticide Regulation (DPR), the Engineering and Laboratory Branch (ELB) of the Air Resources Board (ARB) began conducting application and ambient air sampling in Tulare County, California, during the months of May through July, 1996. This monitoring was conducted to determine the airborne concentrations of the pesticide chlorpyrifos and the chlorpyrifos **oxon** during a three-day application air monitoring study in the vicinity of a treated field during application, and a five-week ambient air monitoring study in populated areas surrounding the application site. The samples were collected by ELB and analyzed by the Trace Analytical Laboratory (TAL), Department of Environmental Toxicology, University of California, Davis.

The Quality Assurance Section (QAS) of the **ARB's** Monitoring and Laboratory Division (MLD) conducted a system audit of the field and laboratory operations to review the sample handling and storage procedures, analytical methodology, and method validation. In general, the laboratory practices were consistent with the Quality Assurance Plan for Pesticide Monitoring (ARB, February 4, 1994).

Additionally, QAS staff conducted performance audits of the air monitoring samplers. The performance audits of the air monitoring samplers were conducted to evaluate the flow rate accuracy. The flow rate audit was conducted on June 17, 1996. The difference between the reported and assigned flow rates for the application air samplers averaged 0.6% and ranged from -1.4% to 3.9%. The difference between the reported and assigned flow rates for the ambient air samplers averaged 2.8% and ranged from 0.8% to 5.5%.

To determine the effectiveness of the analytical procedure, laboratory performance audits were conducted during the study from June 1996 through July 1996. A total of 15 quality assurance (QA) audit samples were spiked with known amounts of **QAS's** standard solution of chlorpyrifos in ethyl acetate and chlorpyrifos **oxon** in ethyl acetate. The 15 audit samples were designated as QA field spikes, QA trip spikes, and QA laboratory spikes. The QA field spikes were exposed to the same handling and storage conditions and also exposed to the same environmental and monitoring conditions as those occurring at the time of ambient sampling. The QA trip spikes followed the same handling and storage conditions of the ambient samples and the QA laboratory spikes were stored at **TAL's** storage freezer and then analyzed at TAL.

The TAL notified **QAS** that while they were analyzing their quality control blank **XAD-4** adsorbent resin and chlorpyrifos fortified XAD-4 adsorbent resin samples, chlorpyrifos

contamination was detected in some blank samples. Since the **XAD-4** adsorbent resin used for the blank samples came from the same lot (bottle) used for the QA audit samples, TAL warned QAS of the possibility that the 15 QA ambient audit samples may also be contaminated. The **TAL's** review of the material records determined that the XAD-4 adsorbent resin was used for the QA samples and for one set of **TAL's** quality control samples.

Analyses of the QA samples were conducted and the results did prove the **XAD-4** adsorbent resin used in the QA sample cartridges were contaminated. Therefore, the QA trip, QA field, and QA laboratory chlorpyrifos spikes results were invalidated. The contaminated adsorbent resin was not used in any of the ambient or application air sample cartridges used for air monitoring.

On July 19, 1996, a make-up batch of ten QA laboratory samples were spiked with known amounts of **QAS's** standard solution of chlorpyrifos in ethyl acetate and chlorpyrifos **oxon** in ethyl acetate. The QA spikes were stored in **TAL's** storage freezer at **-20°** Celsius for three days and were analyzed by TAL on July 22, 1996. The results of the analyses indicate the difference between the assigned and the reported total mass of chlorpyrifos and chlorpyrifos **oxon** averaged 4.8% with a range of -5.3% to 14.9%. After review and discussions with ELB staff, the QA laboratory analytical performance audit data were determined to be reasonable.

## II. CONCLUSION

### Operations

The records for field operations, sample handling procedures, analytical methodology, and method validation were in agreement with the Quality Assurance Plan for Pesticide Monitoring.

### Field Flow Rates

The results of the reported flow rates were in good agreement with the actual flow rates measured by **QAS** staff.

### Laboratory Accuracy

The **first set** of 15 QA analytical performance audit samples were invalidated due to the fact that the XAD-4 adsorbent resin used in the QA sample cartridges were determined to be contaminated with chlorpyrifos. The sample cartridges were assembled by TAL. The **TAL's** review of the material records determined that the XAD-4 contaminated adsorbent resin was

used for the QA samples and for one set of **TAL's** quality control samples. The contaminated adsorbent resin was not used in any of the ambient or application air sample cartridges used for air monitoring.

The second set (make-up batch) of ten QA laboratory audit samples were spiked on July 19, 1996 and were analyzed by TAL on July 22, 1996. The results of the analyses indicate the difference between the assigned and the reported total mass of chlorpyrifos and chlorpyrifos **oxon** averaged 4.8% with a range of -5.3% to 14.9%. After review and discussions with ELB staff, the QA analytical performance audit data were determined to be reasonable.

#### Impact on Data

Since the trip, field, and original laboratory QA audit samples were invalidated due to the chlorpyrifos contamination of the **XAD-4** resin, and additional trip and field QA audit samples were not able to be utilized, the impact on the ambient and application data is unable to be determined.

### III. **RECOMMENDATIONS**

1. The TAL should review laboratory procedures/practices for handling and assembling the sample cartridges. Recommend additional precautions to be established to preclude the possibility of contaminating future sample cartridges.

### IV. **INTRODUCTION**

At the request of the California Department of Pesticide Regulation (DPR), the Engineering and Laboratory Branch (ELB) of the Air Resources Board (ARB) began conducting application and ambient air sampling in Tulare County, California, during the months of May through July, 1996. This monitoring was conducted to determine the airborne concentrations of the pesticide chlorpyrifos and the chlorpyrifos **oxon** during a three-day ambient air monitoring study in the vicinity of a treated field during application and a five-week ambient air monitoring study in populated areas surrounding the application site. The samples were collected by ELB and analyzed by the Trace Analytical Laboratory (**TAL**), Department of Environmental Toxicology, University of California, Davis. The **QAS** staff conducted a system audit of the field and laboratory operations, performance flow audits of the air samplers, and a laboratory performance audit.

## V. AUDIT OBJECTIVE

The system audit was conducted to determine whether the quality control practices for the handling and storage of samples, analytical methodology, and method validation were consistent with the Quality Assurance Plan for Pesticide Monitoring (ARB, February 4, 1994). Performance audits were conducted to evaluate the accuracy of the air samplers' flow rate and the analytical method.

## VI. FIELD AND LABORATORY OPERATIONS

A system audit of the field and laboratory operations was initiated on May 31, 1996, through a questionnaire submitted to TAL staff. Additionally, the Protocol for the Application and Ambient Air Monitoring of Chlorpyrifos (and the **oxon** analogue) in Tulare County During Summer, 1996 and the Standard Operating Procedure for the Analysis of Chlorpyrifos and Chlorpyrifos **Oxon** in Ambient Air were reviewed by QAS staff. In general, the laboratory practices were consistent with the Quality Assurance Plan for Pesticide Monitoring (ARB, February 4, 1994).

### Ambient Air Sampling, Sample Handling and Storage

Samples were collected by drawing ambient air at measured rates through Teflon cartridges containing 30 mL of **XAD-4** adsorbent. An air sampler consisted of the Teflon cartridge connected with Teflon tubing to an in-line rotameter, which in turn was connected to an air pump. The sampling cartridge was protected from the direct sunlight using aluminum foil during the sampling period. The sampling assembly was supported by a two-meter section of galvanized steel tube (Attachment 1).

The samplers' rotameters were set to an indicated flow rate of 15.0 liters per minute (**LPM**). The sampling was conducted following the schedule specified in the sampling protocol. At the completion of each sampling period the cartridges were capped and placed in a zip-lock plastic bag with an identification label affixed. The samples were stored in an ice chest containing dry ice and held in the field for up to four days prior to shipment to TAL.

### Sample Analysis

The analytical method was developed by TAL and described in a document titled "Standard Operating Procedure for the Analysis of Chlorpyrifos and Chlorpyrifos **Oxon** in Ambient

**Air."** The method calls for the **XAD-4** resin to be **desorbed** by shaking with ethyl acetate, the extract volume adjusted, and 3  $\mu\text{L}$  injections made for gas chromatographic determination of the analyte. The injected samples were analyzed on a Hewlett-Packard model 5890 Series II gas chromatograph (GC) equipped with a flame photometric selective detector. A portion of the samples (10% of the samples) were analyzed using gas chromatograph mass spectrology selective ion monitoring to confirm the analyte identity.

The gas chromatograph was calibrated every fifth sample using chlorpyrifos and chlorpyrifos **oxon** standards spanning the concentration range 0.025 to 0.800  $\text{ng}/\mu\text{L}$ . Standard curves consisted of at least five points with triplicate 3  $\mu\text{L}$  injections for each point. Precision checks of the response of each standard calibration data were made to assess instrument precision. Precision showed less than  $\pm 10\%$  difference.

Quality control activities performed to monitor and document the quality of the data included analysis of a field control blank with every sample shipment, field spikes when time permitted, laboratory blanks, and field duplicates from collocated sites once per sampling period.

#### Method Validation

The limit of detection (LOD) was calculated as 0.20  $\mu\text{g}$ . Trapping efficiency was determined to be an average 82~5.4% for chlorpyrifos and **74 $\pm$ 8%** for the chlorpyrifos **oxon**. A sample storage stability study was conducted to determine the percent recovery for 50  $\mu\text{g}$  chlorpyrifos and chlorpyrifos **oxon** samples stored in a **-20°** Celsius freezer. The results of the stability study shows the chlorpyrifos samples had an average 92% recovery with a standard deviation of 3.2% for a **37-day** storage period. The chlorpyrifos **oxon** samples had an average 100% recovery with a standard deviation of 1.0% for a **31-day storage period**. No breakthrough occurred during the 24 hours of dynamic sampling at 30 LPM air flow.

#### Documentation

All the samples received at the laboratory were accompanied by chain-of-custody records. Field data sheets containing the sample collection information were retained by ELB. The information recorded in the field data sheets included sampler ID, sampling date, start and stop times, flow rate, and comments about unusual conditions.



Laboratory and instrument maintenance logs were kept in bound notebooks with numbered pages. The entries made in the laboratory book included sample number, sample type, date sample was received, collection date, date of analysis, results of analysis, and analyst.

The raw analytical data were recorded on electronic files and will be kept for four years by **TAL**.

## VII. PERFORMANCE AUDITS

### Flow Rate Audit

On May 30, 1996, the flow rate of each sampler used for the monitoring was audited for the application air samplers and on July 17, 1996, for the ambient air samplers, following the procedures outlined in Attachment 2. The audit was conducted with a 0 to 3 LPM mass flow meter traceable to the National Institute of Standards and Technology (**NIST**). The difference between the reported and true flow rates for the application air samplers averaged 0.6% and ranged from -1.4% to 3.9% (Table 1). The difference between the reported and true flow rates for the ambient air samplers averaged 2.8% and ranged from 0.8% to 5.5% (Table 2).

Table 1

Results of the Flow Audit Conducted on the  
Application Samplers Used during the Monitoring  
for Chlorpyrifos and Chlorpyrifos Oxon

Sampler Number	Reported Flow (LPM)	True Flow (LPM)	Percent Difference
=====	=====	=====	=====
1	14.5	14.52	-0.1
2	14.5	14.70	-1.4
3	14.5	13.95	3.9
4	14.5	14.55	-0.3
5	14.5	14.37	0.9

**NOTE :** The percent difference calculated by using the following equation:

$$\frac{\text{Reported Flow} - \text{True Flow}}{\text{True Flow}} \times 100$$

Table 2

Results of the Flow Audit Conducted on the  
Samplers Used during the Monitoring  
for Chlorpyrifos and Chlorpyrifos **Oxon**

Sampler Number	Reported Flow (LPM)	True Flow (LPM)	Percent Difference
1	14.67	14.23	3.1
2	14.67	14.45	1.5
3	14.67	14.55	0.8
4	14.67	14.34	2.3
5	14.67	14.34	2.3
6	14.67	14.91	5.5
7	14.67	14.12	3.9
8	14.67	14.12	3.9
9	14.67	14.55	0.8
10	14.67	14.12	3.9

NOTE : The percent difference calculated by using the  
following equation:

$$\frac{\text{Reported Flow} - \text{True Flow}}{\text{True Flow}} \times 100$$

#### Analytical Performance Audit

A total of 15 QA ambient audit samples were spiked with known amounts of the **QAS's** standard solution of chlorpyrifos in ethyl acetate and chlorpyrifos **oxon** in ethyl acetate following the procedures outlined in Attachment 3. The QA audit samples were spiked at TAL and transferred to different locations for exposure to various audit conditions. The QA audit samples were designated as QA field spikes, QA trip spikes, and QA laboratory spikes. The QA field spikes were exposed to the same handling and storage conditions and also exposed to the same environmental and monitoring conditions as those occurring at the time of ambient sampling. The QA trip spikes followed the same handling and storage conditions of the ambient samples. The QA laboratory spikes were stored at **TAL's** storage freezer and then analyzed.

The TAL notified **QAS** that while they were analyzing their blank **XAD-4** adsorbent resin and chlorpyrifos-fortified XAD-4 adsorbent resin samples, chlorpyrifos contamination was detected in some of the blank samples. Since the **XAD-4 adsorbent** resin used for the blank samples came from the same lot (bottle) used for the QA audit samples, **TAL** warned **QAS** of the possibility that the 15 QA ambient audit samples may also

be contaminated. The **TAL's** review of the material records" determined that this XAD-4 resin bottle was used for the QA samples and for one set of **TAL's** quality control samples. The contaminated adsorbent resin was not used in any of the sample cartridges used for application or ambient air monitoring. Therefore, the contamination did not impact the ambient data.

The five ambient QA trip spikes were exposed to the same handling and storage conditions as those occurring at the time of ambient monitoring. The trip spikes were shipped in an ice chest containing dry ice from the TAL laboratory to the ARB ambient air monitoring station located in Visalia. At the Visalia site, the trip spikes were stored for four days in an ice chest containing dry ice, packaged with the ambient QA field spikes and shipped to TAL for analysis.

The ambient QA trip spikes were analyzed on June 20, 1996. The results of the QA trip spike analyses indicate the difference between the assigned and the reported total mass of chlorpyrifos averaged 106.3% with a range of -27.0% to **232.0%** (Table 3). **The analytical** results have shown the XAD-4 adsorbent resin used in the QA sample cartridges were contaminated. Therefore, the QA trip spikes results were invalidated.

Table 3

Results of Analyses of the QA Trip Spikes  
Chlorpyrifos and Chlorpyrifos Oxon  
in Ethyl Acetate

Sample ID	Assigned Mass (μg)		Reported Mass (μg)		Percent Difference
	Chlor-pyrifos	Chlor-pyrifos Oxon	Chlor-pyrifos	Chlor-pyrifos Oxon	
QA-1B	2.5	2.5	4.64	2.19	36.6
QA-2B	2.5	2.5	1.96	1.69	-27.0
QA-3B	0.5	0.0	0.98	co.20	96.0
QA-4B	0.5	0.0	1.47	co.20	194.0
QA-5B	0.0	0.5	0.22	1.44	232.0

NOTE: The percent difference is calculated by using the following equation:

$$\frac{\text{Reported Mass} - \text{Assigned Mass}}{\text{Assigned Mass}} \times 100$$

The five ambient QA field spikes were transported with the ambient QA trip spikes in the same ice chest containing dry ice to the ARB ambient air monitoring station located in Visalia. The QA field spikes were installed into the pesticide air monitor at this station and exposed to 24 hours of ambient air sampling through the tube samples at a rate of 15 LPM. A replicate air sampler (collocated) was used to collect and determine the background ambient air concentrations. After exposure to the field conditions, the samples were packaged, stored, and shipped in an ice chest containing dry ice to TAL for analysis.

The QA field spikes were also analyzed by TAL on June 20, 1996. After correcting for the background ambient air concentrations, the analytical results indicate the difference between the assigned and the reported total mass of chlorpyrifos for the QA field spikes averaged -7.0% with a range of -23.0% to 4.3% (Table 4). The analytical results have shown the XAD-4 adsorbent resin used in the QA sample cartridge identified as QA-2A was contaminated. Since the XAD-4 adsorbent resin used for the blank samples came from the same lot (bottle) used for the QA audit samples, the QA field spikes results were invalidated,

Table 4  
Results of Analyses of the QA Field Spikes  
Chlorpyrifos and Chlorpyrifos Oxon  
in Ethyl Acetate

Sample ID	Assigned Mass ( $\mu\text{g}$ )	Reported Mass ( $\mu\text{g}$ )	Percent Difference
	Chlor-pyrifos	Chlor-pyrifos Oxon	
QA-1A	5.0	4.89 <sup>1</sup>	4.3
QA-2A	0.0	1.02 <sup>1</sup>	
QA-3A	1.0	0.77 <sup>1</sup>	-23.0
QA-4A	150.0	136.0 <sup>1</sup>	-6.2
QA-5A	50.0	46.0 <sup>1</sup>	-3.1

- 1: No background concentrations detected.  
 2: Corrected for background concentration of 0.32  $\mu\text{g}$  chlorpyrifos.  
 3: Corrected for background concentration of 0.34  $\mu\text{g}$  chlorpyrifos oxon.  
 4: Corrected for background concentration of 0.24  $\mu\text{g}$  chlorpyrifos oxon.

NOTE: The percent difference is calculated by using the following equation:

$$\frac{\text{Reported Mass} - \text{Assigned Mass}}{\text{Assigned Mass}} \times 100$$

On July 19, 1996, a make-up batch of ten QA laboratory samples (identified as QA-1L to QA-10L) were spiked with known amounts of the QAS's standard solution of chlorpyrifos in ethyl acetate and chlorpyrifos oxon in ethyl acetate following the procedures outlined in Attachment 3. The QA spikes were stored in TAL's storage freezer at -20° Celsius, along with the suspected contaminated QA Laboratory spikes identified as QA-1C to QA-5C. The QA laboratory spikes (QA-1C to 5C and QA-1L to 10L) were analyzed by TAL on July 22, 1996.

The results of the analyses for the five QA laboratory samples, QA-1C through QA-5C, indicate the difference between the assigned and the reported total mass of chlorpyrifos and chlorpyrifos oxon averaged 4.4% with a range of 0.1% to 7.5% (Table 5). The analysis results have shown the XAD-4 adsorbent resin used for QA audit sample cartridge identified as QA-3C was contaminated. Since the XAD-4 adsorbent resin used for the blank samples came from the same lot (bottle). used for the QA audit samples, the QA laboratory spikes results were invalidated.

Table 5  
Results of Analyses of the Five QA Laboratory Spikes  
Chlorpyrifos and Chlorpyrifos Oxon  
in Ethyl Acetate

Sample ID	Assigned Mass (µg)		Reported Mass (µg)		Percent Difference
	Chlor-pyrifos	Chlor-pyrifos Oxon	Chlor-pyrifos	Chlor-pyrifos Oxon	
QA-1C	5.0	1.0	5.04	1.21	4.2
QA-2C	5.0	1.0	5.33	1.12	7.5
QA-3C	0.0	0.0	2.96	co. 20	
QA-4C	200.0	20.0	200.12	20.16	0.1
QA-5C	5.0	1.0	5.05	1.29	5.7

NOTE: The percent difference is calculated by using the following equation:

$$\frac{\text{Reported Mass} - \text{Assigned Mass}}{\text{Assigned Mass}} \times 100$$

The results of the analyses for the ten make-up QA laboratory samples, **QA-1L** through **QA-10L**, indicate the difference between the assigned and the reported total mass of chlorpyrifos and chlorpyrifos **oxon** averaged 4.8% with a range of -5.3% to 14.9% (Table 6). After review and discussions with ELB staff, the ten make-up QA laboratory performance audit data were determined to be reasonable.

Table 6

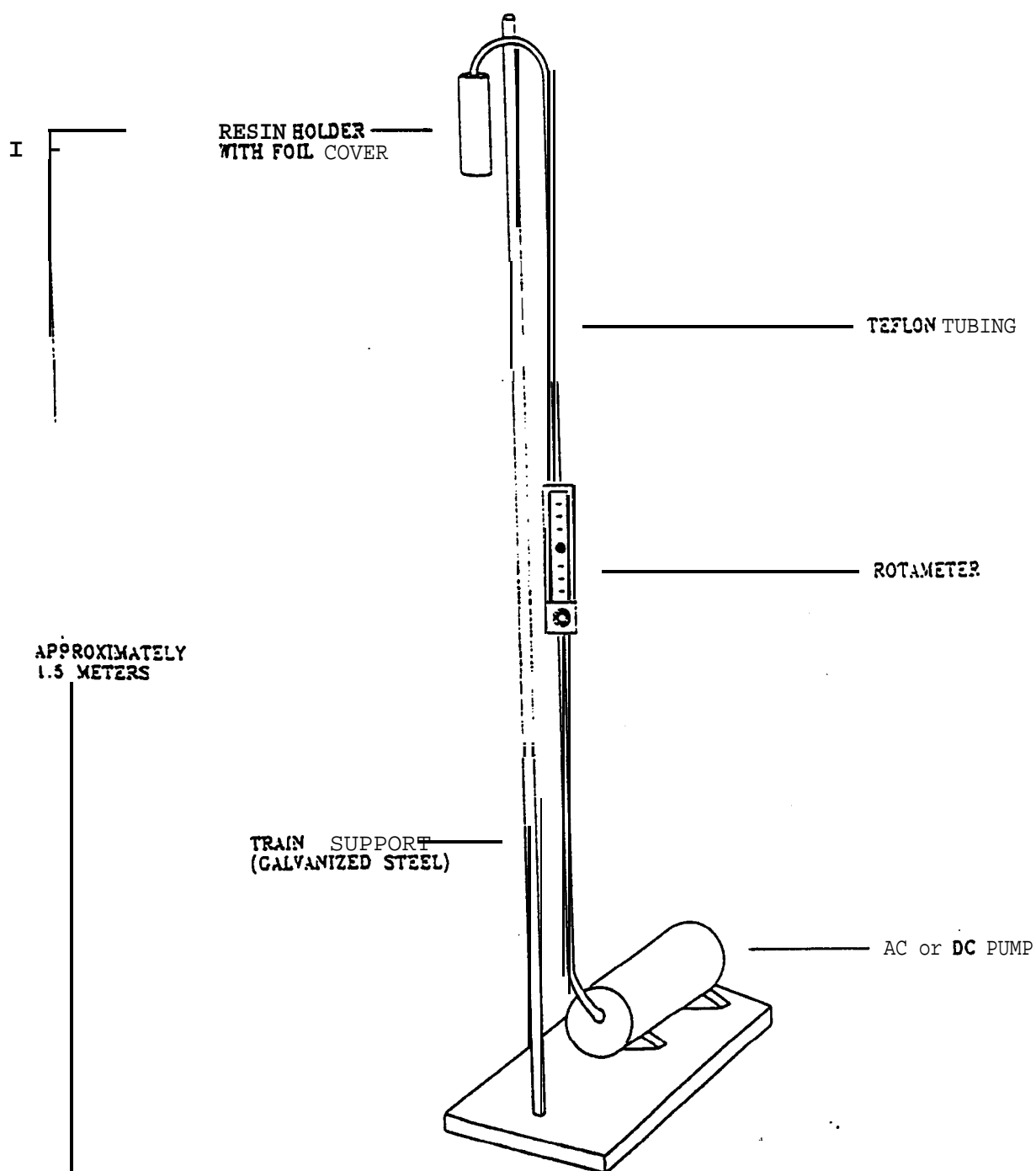
Results of Analyses of the Make-up QA Laboratory Spikes  
Chlorpyrifos and Chlorpyrifos **Oxon**  
in Ethyl Acetate

Sample ID	Assigned Mass ( $\mu\text{g}$ )		Reported Mass ( $\mu\text{g}$ )		Percent Difference
	Chlor-pyrifos	Chlor-pyrifos Oxon	Chlor-pyrifos	Chlor-pyrifos Oxon	
<b>QA-1L</b>	5.0	2.5	<b>5.82</b>	2.80	14.9
QA-2L	<b>1.0</b>	<b>0.0</b>	<b>1.08</b>	<b>&lt;0.20</b>	8.0
QA-3L	5.0	2.5	5.41	3.01	12.3
QA-4L	1.0	0.0	<b>1.01</b>	co. 20	<b>1.0</b>
<b>QA-5L</b>	<b>0.0</b>	<b>0.0</b>	co. 20	co. 20	
QA-6L	<b>10.0</b>	<b>0.0</b>	10.36	co. 20	3.6
QA-7L	<b>10.0</b>	5.0	9.95	5.51	3.1
QA-8L	25.0	5.0	23.48	4.94	-5.3
<b>QA-9L</b>	25.0	<b>10.0</b>	24.58	10.68	0.7
<b>QA-10L</b>	50.0	50.0	50.99	53.71	4.7

**NOTE:** The percent difference is calculated by using the following equation:

$$\frac{\text{Reported Mass} - \text{Assigned Mass}}{\text{Assigned Mass}} \times 100$$

AIR SAMPLER USED IN THE MONITORING OF CHLORPYRIFOS



FLOW RATE AUDIT PROCEDURES FOR AIR SAMPLERS  
USED IN PESTICIDE MONITORING

..

### Introduction

Air samplers are audited using a calibrated differential pressure gauge or a mass flow meter that is standardized against a National Institute of Standards and Technology (NIST) traceable flow calibrator. The audit device is connected in series with the sampler's flow meter. The flow rate is measured while the sampler is operating under normal sampling conditions. The sampler's indicated flow rate is corrected based on its calibration, and the true flow is calculated from the audit device's calibration curve. The sampler's reported flow is compared to the true flow, and a percent difference is determined.

### Equipment

The basic equipment required for the air sampler flow audit is listed below. Additional equipment may be required depending on the particular configuration and type of sampler.

1. NIST-traceable mass flow meter.
2. Calibrated differential pressure gauge with laminar flow element.
3. 1/4" O.D. Teflon tubing.
4. 1/4", stainless steel, Swagelock fittings.

### Audit Procedures

1. If power is available, connect the mass flow meter into a 110 VAC outlet, and allow it to warm up for at least ten minutes. Otherwise, perform the audit with the calibrated differential pressure gauge.
2. Connect the inlet port of the audit device to the outlet port of the sampler's flow control valve with a five-foot section of Teflon tubing and Swagelock fittings.
3. Connect the outlet port of the audit device to the pump with another five foot section of Teflon tubing and Swagelock fittings.
4. Allow the flow to stabilize for at least one to two minutes and record the flow rate indicated by the sampler and audit device's response.



5. Calculate the true flow rate from the audit device's response and record the results. Obtain the corrected sampler flow rate from the field operator. Calculate the percent difference between the true flow rate and the reported flow rate.

The percent difference is calculated by using the following equation:

$$\frac{\text{Reported Flow} - \text{True Flow}}{\text{True Flow}} \times 100$$

**PERFORMANCE AUDIT PROCEDURES  
FOR THE LABORATORY ANALYSIS  
OF CHLORPYRIFOS AND CHLORPYRIFOS OXON**

Introduction

The purpose of the laboratory performance audit is to assess the accuracy of the analytical method used by the laboratory to measure the ambient concentrations of chlorpyrifos and chlorpyrifos **oxon**. The audit is conducted by submitting audit samples spiked with known concentrations of chlorpyrifos and chlorpyrifos **oxon**. The analytical laboratory reports the results to the Quality Assurance Section. The difference between the reported and the assigned concentrations is used as an indicator of the accuracy of the analytical method.

Materials

1. chlorpyrifos, 10.0  $\mu\text{g/mL}$  chlorpyrifos in ethyl acetate, Chem Service, Lot #175-11B. (Chem Ser.)
2. chlorpyrifos, 10.0  $\mu\text{g/mL}$  chlorpyrifos in ethyl acetate, AccuStandard Inc., Lot #066-080. (AccuStd)
3. chlorpyrifos, 1.00  $\text{mg/mL}$  chlorpyrifos in ethyl acetate, Chem Service, Trace Analytical Laboratory (TAL), Department of Environmental Toxicology, University of California, Davis. Lot #3-23-96. (TAL #3)
4. chlorpyrifos **oxon**, 10.0  $\mu\text{g/mL}$  chlorpyrifos **oxon** in ethyl acetate, TAL, Lot #6-3-96. (TAL #4)
5. chlorpyrifos **oxon**, 100.0  $\mu\text{g/mL}$  chlorpyrifos **oxon** in ethyl acetate, TAL, Lot #06-03-96. (TAL #5)
6. XAD-4 adsorbent resin cartridges, supplied by TAL.

Safety Precautions

Prior to handling any chemical, read the manufacturer's Material Safety Data Sheets (MSDS). Avoid direct physical contact with chemicals. Avoid breathing vapors. Use only under a fume hood. Wear rubber gloves, safety glasses, and protective clothing.

Prewaration of Audit Samples

Prepare five trip samples, five field samples, and five laboratory audit samples by spiking the XAD-4 adsorbent cartridges with the volume of chlorpyrifos and chlorpyrifos **oxon** spiking solution indicated in Table 1 below. Using a microsyringe, insert the needle into the primary section of the XAD-4 cartridge, and push the plunger slowly while spiking the XAD-4 adsorbent resin.

Table 1  
Volume of Chlorpyrifos and Chlorpyrifos **oxon** .  
in Ethyl Acetate Used to Spike the  
QA Ambient Audit Samples

Sample ID	Standard Solution Supplier	Chlorpyrifos Spiking Solution Volume (mL)	Standard Solution Supplier	Chlorpyrifos <b>Oxon</b> Spiking Solution Volume (mL)
<b>Field Spikes</b>				
<b>QA-1A</b>	Chem Ser.	<b>0.50</b>	TAL #4	0.25
QA-2A	-S <sub>w</sub> --	0.00	-----	0.00
QA-3A	AccuStd	0.10	-----	0.00
QA-4A	TAL #3	0.15	TAL #5	0.20
<b>QA-5A</b>	TAL #3	0.05	TAL #5	0.75
<b>Triw Spikes</b>				
<b>QA-1B</b>	Chem Ser.	0.25	TAL #4	0.25
QA-2B	AccuStd	0.25	<b>TAL #4</b>	0.25
QA-3B	AccuStd	0.05	m--e-	0.00
QA-4B	Chem Ser.	0.05	-----	0.00
<b>QA-5B</b>	-----	0.00	TAL #4	0.05
<b>Laboratory Swikes</b>				
<b>QA-1C</b>	Chem Ser.	0.50	<b>TAL #4</b>	0.10
QA-2C	Chem Ser.	<b>0.50</b>	<b>TAL #4</b>	0.10
QA-3C	-----	0.00	-----	0.00
<b>QA-4C</b>	<b>TAL #3</b>	0.20	TAL #5	0.20
QA-SC	AccuStd	0.50	<b>TAL #4</b>	0.10

Prepare ten make-up laboratory audit samples by spiking the **XAD-4** adsorbent cartridges with the volume of **chlorpyrifos** and chlorpyrifos **oxon** spiking solution indicated in Table 2 below. Using a microsyringe, insert the needle into the primary section of the **XAD-4** cartridge, and push the plunger slowly while spiking the **XAD-4** adsorbent resin.

Table 2  
Volume of Chlorpyrifos and Chlorpyrifos **oxon**  
in Ethyl Acetate Used to Spike the  
QA Ambient Audit Samples

Sample ID	Standard Solution Supplier	Chlorpyrifos Spiking Solution Volume (mL)	Standard Solution Supplier	Chlorpyrifos <b>Oxon</b> Spiking Solution Volume (mL)
=====				
<b>Laboratory Spikes</b>				
<b>QA-1L</b>	Chem Ser.	0.50	<b>TAL #4</b>	0.25
QA-2L	Chem Ser.	0.10	-----	0.00
QA-3L	<b>AccuStd</b>	0.50	<b>TAL #4</b>	0.25
QA-4L	<b>AccuStd</b>	<b>0.10</b>	e-B--	0.00
QA-5L	-----	0.00	-----	0.00
QA-6L	<b>TAL #3</b>	0.01	-----	0.00
QA-7L	TAL #3	0.01	TAL #5	0.05
<b>QA-8L</b>	TAL #3	0.025	TAL #5	0.05
<b>QA-9L</b>	<b>TAL #3</b>	0.025	<b>TAL #5</b>	0.10
<b>QA-10L</b>	TAL #3	0.05	TAL #5	0.50

## APPENDIX IV

### PCA'S APPLICATION RECOMMENDATIONS

PEST MANAGEMENT ASSOCIATES

P.O. Box 712

Exeter, CA 93221

209-592-7461

FORM: # 970745

DATE: 05-28-97

EXPIRATION DATE: 06-10-97

PROPOSED APPL DATE: 05-30-97

COMPLETED DATE: -----

POSTING REQUIRED: no

GROWER: Permit 54-97-1500573

Paramount Citrus

36445 Rd 172

Visalia, CA 93292

PERMIT REQUIRED: ~~yes~~ NONOT REQUIRED: ~~yes~~ NO

DAYS TO HARVEST: 35

DAYS TO REENTRY: 2

COMMODITY: Oranges

RANCH : Rayo

LOCATION: NW Ave 360 and Rd 172

SW Ave 360 and Rd 172

COUNTY: 54 SECTION: 18 TOWNSHIP: 17 S RANGE: 26 E BASE &amp; MERIDIAN:

COUNTY: 54 SECTION: 19 TOWNSHIP: 17 S RANGE: 26 E BASE &amp; MERIDIAN:

SITE IDs: 33-102A 33-103 33-107

BLOCKS: 25N 25S 28 31  
32 32Y

ACRES : 117.23

REASON: Pest Present

PESTS: California Red Scale

MATERIAL	RATE PER ACRE		VOL IN AMOUNT PER		TOTAL	
			GAL/ACRE	500 GAL TANK	MATER:	
LORSBAN	4E	12.00 pts	750.00	8.00 pts	175.94	g

APPLY BY: Ground - MAXIMUM SPEED: 1.00 MPH - CONCENTRATION: Dilute

COMMENTS FOLLOW COMPLETE LABEL INSTRUCTIONS

do not treat if air temperature is above 90 deg F

confine spray to target area

thorough coverage is necessary

ad Just pH of spray tank to 7.0

I certify that I have considered alternatives and mitigation measures that would substantially lessen any significant impact on the environment, and have adopted those found feasible.

PCA : #3125

Sylvie Robillard

SIGNATURE: 

PEST MANAGEMENT ASSOCIATES

P.O. Box 712

Exeter, CA 93221

209-592-9461

GROWER: Permit 54-97-1500573

Paramount Citrus

36445 Rd 172

Visalia, CA 93292

FORM: it 370666

DATE: 05-13-97

EXPIRATION DATE: 06-01-97

PROPOSED APPL DATE: 05-15-97

COMPLETED DATE: -----

POSTING REQUIRED: no

PERMIT REQUIRED: no

NOI REQUIRED: no

DAYS TO HARVEST: 3 5

DAYS TO REENTRY: 2

COMMODITY: Oranges

RANCH: Rayo

LOCATION: NW Ave 360 and Rd 172

COUNTY: 54 SECTION: 18 TOWNSHIP: 17 S RANGE: 26 E BASE &amp; MERIDIAN:

COUNTY: 54 SECTION: 17 TOWNSHIP: 18 S RANGE: 26 E BASE &amp; MERIDIAN:

SITE IDs: 33-103 33-105

BLOCKS: 11	15	16	17
20	21	22	23
24	26	26Y	23
30			

ACRES: 361.78

REASON: Pest Present

PESTS: California Red Scale

MATERIAL	RATE PER ACRE	VOL IN GAL/ACRE	AMOUNT PER 500 GAL TANK	TOTAL MATERIAL
LORSBAN 4E	12.88 pts	758.80	a.00 pts	572.67 g

APPLY BY: Ground - MAXIMUM SPEED: 1.00 MPH - CONCENTRATION: Dilute

COMMENTS FOLLOW COMPLETE LABEL INSTRUCTIONS

do not treat if air temperature is above 30 deg F

confine spray to target area

thorough coverage is necessary

adjust pH of spray tank to 7.0

I certify that I have considered alternatives and mitigation measures that would substantially lessen any significant impact on the environment, and have adopted those found feasible.

PCA : #3125

Sylvie Robillard

SIGNATURE: 

106

APPENDIX V

DPR'S MONITORING RECOMMENDATION  
FOR CHLORPYRIFOS



## M e m o r a n d u m

**To** Genevieve Shiroma, Chief  
Toxic Air Contaminant Identification Branch  
Air Resources Board  
P.O. Box 2815  
Sacramento, California 95812

**Date** : April 28, 1995

**Place** :

**From** **Department of Pesticide Regulation** — 1020 N Street, Room 161  
Sacramento, California 958145624

**Subject** Monitoring Recommendation for Chlorpyrifos.

In order to fulfill the requirements of **AB 1807/3219** (Food and **Agricultural Code, Division 7**, Chapter 3, Article **1.5**), the Department of Pesticide Regulation (**DPR**) requests that the Air Resources Board (**ARB**) document the airborne concentrations of **the pesticide chlorpyrifos [O,O-diethyl O-(3,5,6-trichloro-2-pyridinyl) phosphorothioate]**. This memorandum **provides** background and recent use information on chlorpyrifos containing products, and identifies how they are used.

Technical chlorpyrifos is a crystal, white to amber in color with a mild mercaptan-like odor. Chlorpyrifos has a molecular weight of 350.59 g/mole and a specific density of 1.398 at 43.5 °C. It has a water **solubility** of 450,730, and 1,300 µg/L at 10, 20, and 30 °C respectively, a Henry's constant of  $4.16 \times 10^{-6} \text{ atm} \cdot \text{m}^3$ , and a vapor pressure of  $1.7 \times 10^{-5} \text{ mmHg}$  at 25 °C. The half-life ( $t_{1/2}$ ) of chlorpyrifos in several environmental compartments is: 1) Soil  $t_{1/2}$  varies from 12 weeks to 1 day depending on soil type and soil temperature; 2) Surface water (**estuarine**)  $t_{1/2}$  24 days; and 3) Surface water (fresh, 25 °C)  $t_{1/2}$  varies from 120 days (**pH** 6.1) to 53 days (**pH** 7.4). Photolytic  $t_{1/2}$  in freshwater at 40° N latitude (depth  $10^3$  cm) is reported as 31 days during midsummer and 345 days at midwinter. Increasing the depth to 1 meter increased photolytic  $t_{1/2}$  to 2.7 years.

The acute oral LD<sub>50</sub> of chlorpyrifos for male and female rats is 163 and 135 mg/kg respectively. The LC<sub>50</sub> (96 hour) for rainbow trout is 3 µg/L, for bluegill sunfish 2.6µg/L, and for an **estuarine** mysid 0.035 µg/L. The OSHA 8-hour time weighted average for a personal exposure limit is 0.2 mg/m<sup>3</sup>. Chlorpyrifos **has entered the risk assessment** process at DPR under the SB 950 (Birth Defect Prevention Act of 1984) based on its mutagenicity and on its relatively low NOEL (No-Observed-Effect-Level).

**AS** of April 3, 1995, there were 468 active registrations for products containing chlorpyrifos. These products consist of flea and tick collars for dogs, home use products for the control of lawn insects and termites, and agricultural products. Formulations of chlorpyrifos include impregnated plastics (flea collars), granular, emulsifiable concentrations, wettable powders, dusts, **flowables**, and **microcapsules**. **Common** trade names are **Lorsban®** and **Dursban®**. The **Signal** Words on agricultural products are Warning (**Lorsban® 4C, 50W**) and Caution (**Lorsban® 15G**).



The following table summarizes the 1993, 1992 and 1991 Pesticide Use Report (PUR) data for chlorpyrifos in pounds active ingredient (AI).

Table 1: **Chlorpyrifos Use** by Year. (Pounds of Active Ingredient)

County	1993	1992	1991
<b>Fresno</b>	179,011.3	175,734.7	107,860.3
<b>Imperial</b>	101,486.3	105,048.3	146,046.1
<b>Kern</b>	160,191.4	165,295.5	116,007.7
<b>Los Angeles</b>	153,570.1	143,573.1	131,500.1
<b>Orange</b>	100,366.8	2 19,679.4	90,257.5
<b>son Diego</b>	62,670.6	101,243.4	107,128.1
<b>San Joaquin</b>	102,641.7	111,741.3	95,054.8
<b>Santa Clara</b>	67,595.7	124,184.6	103,906.0
<b>stamislus</b>	117,876.3	119,935.8	129,789.1
<b>Tulare</b>	3 10,977.2	421,268.6	229,928.9
County Totals	1,356,387.4	1,687,704.7	1,257,478.6
TOTAL CA USE	2,287,737.4	2,592,509.6	2,097,085.0

The PUR data summed in Table 1 show that the largest applications of chlorpyrifos routinely occur in **Tulare** County. Additionally, these data show that the greatest applications generally occur during May, June and July of each year (**Table 2**). In 1993, chlorpyrifos was applied to almonds at rates of 1.7 to 2.3 lbs active ingredient (AI)/acre during July, and in other counties in amounts similar to those in Table 2 but at application rates 0.6 to 2.8 lbs AI/acre. Application rates for chlorpyrifos during the months of October through April range from 0.25 to 1.5 lbs AI/acre.

Table 2. **Chlorpyrifos** applications in Tulare County (Pounds of **Active** Ingredient)

Tulare County	1993	1992	1991
<b>May (lbs AI)</b>	63,659.1	45,718.1	11,567.2
(Rate)	5.0	4.4	1.8
<b>June (lbs AI)</b>	65,696.0	96,372.6	57,611.0
(Rate)	3.7	5.3	4.7
<b>July (lbs AI)</b>	50,233.3	63,302.0	42,761.1
(Rate)	5.5	4.7	5.2

Chlorpyrifos is used in the San Joaquin Valley on Oranges to control Lepidopterous pests (fruittree leafroller, orange **tortrix**, omnivorous leafroller), scale (California Red and California Yellow armored scale, brown soft scale, citricola scale), mites, ants, and mealy bugs.

Chlorpyrifos applications are made beginning in late-March and extend throughout October, peaking in June. Occasionally, chlorpyrifos is applied to citrus in Tulare County during August. However, while the total amount applied may **be** similar to amounts applied from May through July, the application rate is less, approximately 1.5-2.0 lbs AI/acre.

## **RECOMMENDATIONS:**

### **Ambient Air Monitoring.**

The use patterns for chlorpyrifos suggests that monitoring should take place in Tulare County during a **30- to 45-day** sampling period in the months of May, June, or July. 'Three to five sampling sites should be selected in relatively high-population areas or in areas frequented by people. Sampling sites should be in Orange growing areas but not immediately adjacent to orange groves. At each site, twenty to thirty discrete **24-hour** samples should be taken during the sampling period. Background samples should be collected in an area distant to chlorpyrifos applications.

Replicate (co-located) samples are needed for five dates at each sampling location. Two co-located samplers (in addition to the primary sampler) should be run on those days. The date chosen for replicate samples should be distributed over the entire sampling period. They may; but need not be, the same dates at every site. Field blank and spike samples should be collected at the same environmental (temperature, humidity, exposure to sunlight) and experimental (air flow rates) conditions as those occurring at the time of ambient sampling.

### **Monitoring of an Application Site.**

The use pattern for chlorpyrifos suggests that application-site monitoring should be conducted during the months of May, June, or July in Tulare County, and that the application be associated with Oranges. Due to the extensive use of chlorpyrifos on Oranges during this period, care should be taken so that other applications to nearby groves during the sampling period do not affect sample collection. A three day monitoring period should be established with sampling times as follows. Application + 1 hour, followed by one 2-hour sample, one **4-hour** sample, two **8-hour** samples and two **24-hour** samples. A minimum of four samplers should be positioned, one on each side of the field. A fifth sampler should be co-located at one **position**. Since chlorpyrifos is extensively used in the area, background samples should collect enough volume (either **12** hours at **15 liters/min.**, or a shorter period with a higher volume pump) to permit a reasonable minimum detection level. Ideally samplers should be placed a minimum of 20 meters **from** the field. Field blank and field spike samples **should** be collected at the same **environmental**

Genevieve Shiroma

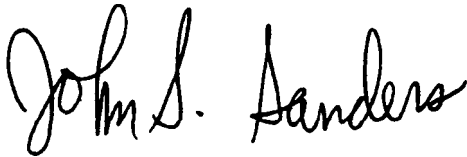
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(temperature, humidity, exposure to sunlight) and experimental (similar air flow rates) conditions as those occurring at the time of sampling.

We also request that you provide in the monitoring report: 1) An accurate record of the positions of the monitoring equipment with respect to the field, 2) an accurate drawing of the, monitoring site showing the precise location of the meteorological equipment, trees, buildings, — etc., 3) meteorological data collected at a minimum of 15 minute intervals **including** wind speed and direction, humidity, and comments regarding degree of cloud cover, and **4)** the elevation **of** each sampling station with respect to the field, and the orientation of the **field** with respect to North (identified as either true or magnetic North).

If you have any questions please contact Kevin **Kelley**, of my staff, at (916) 3244187.



John S. Sanders, Chief  
Environmental Monitoring and Pest Management  
Department of Pesticide Regulation, Room 161  
(916) 3244100

cc: Paul **Gosselin**, DPR  
John Donahue, DPR  
Barry **Cortez**, DPR  
Jay **Schneider**, DPR  
Kevin Kelley, DPR  
Leonard Craft Jr., **Tulare** County  
Agricultural Commissioner

Chuck **Andrews**, DPR  
Gary Patterson, DPR  
Madeline Ames, DPR  
**Lynn** Baker, ARB  
Ruth Tomlin, ARB  
George Lew, ARB

**APPENDIX VI**  
**APPLICATION AND AMBIENT**  
**FIELD LOG SHEETS**

**LOG BOOK**  
Project **C96-032/041**  
Chlorpyrifos, ambient

log number	sample ID	date	time	comments	weather o-overcast bc=partly cloudy ic-clear	taken by
1	ARB-1	5/28/96	1200		K	KEM
		5/29/96	1130		K	
2	J-1	5/29/96	1230		K	KEM
		5/29/96	1300		K	
3	S-1	5/28/96	1300		K	KEM
		5/29/96	1330		K	
4	K-1	5/28/96	1400		K	KEM
		5/29/96	1400		K	
5	UC-1	5/28/96	1430		K	KEM
		5/29/96	1430		K	
6	ARB-2	5/29/96	1130		K	KEM
		5/30/96	1000		K	
7	ARB-20	5/29/96	1130	Days	K	KEM
		5/30	1000		K	
8	J-2	5/29/96	1300		K	KEM
		5/30	1000	1100	K	
9	J-20	5/29/96	1300	Days	K	KEM
		5/30	1000	1100	K	
10	S-2	5/29/96	1330		K	KEM
		5/30	1130		K	
11	S-20	5/29/96	1330	Days	K	KEM
		5/30	1130		K	
12	K-2	5/29	1400		K	KEM
		5/30	1200		K	
13	K-20	5/29	1400	Days	K	KEM
		5/30	1200		K	
14	UC-2	5/29	1430		K	KEM
		5/30	1300		K	
15	UC-20	5/29	1430	Days	K	KEM
		5/30	1300		K	
16	B-1	5/29	1430	Blank	K	KEM
		5/29			K	
17	ARB-3	5/30	1000		K	
		5/31	1130		K	
18	J-3	5/30	1000	1100	K	
		5/31	1030		K	
19	S-3	5/30	1130		K	
		5/31	1100		K	
20	K-3	5/30	1200		K	
		5/31	1000		K	
21	UC-3	5/30	1300		K	
		5/31	0930		K	
2	2				K	

**LOG BOOK**  
 Project **C96-032/041**  
 Chlorpyrifos, ambient

log number	sample ID	date	time	comments	weather o-overcast pc-partly cloudy k-clear taken by
23	ARB1	6-29-96	1200		K NTA
24	K1	6-29-96	1235		K NTA
25	S1	6-29-96	1330		K NTA
26	J1	6-29-96	1415		K NTA
27	UC1	6-29-96	1500		K NTA
28	ARB-2	6-30-96	1000		K NTA
29	K2	6-30-96	1045		K NTA
30	S2	6-30-96	1230		K NTA
31	J2	6-30-96	1250		K NTA
32	UC2	6-30-96	1330		K NTA
33	ARB3	6-30-96	0900		K NTA
34	K3	6-30-96	0945		K NTA
35	S3	6-30-96	1015		K NTA
36	J3	6-30-96	1200		K NTA
37	UC3	6-30-96	1230		K NTA
38	ARB4	6-30-96	0900		K NTA
39	ARB4D	6-30-96	0900		K NTA
40	K4	6-30-96	0945		K NTA
41	K4D	6-30-96	0945		K NTA
42	S4	6-30-96	1015		K NTA
43	S4D	6-30-96	1015		K NTA
44	J4	6-30-96	1100		K NTA

## LOG WORK

Project **C96-032/041**  
Chlorpyrifos, ambient

weather  
o=overcast  
pc=partly cloudy  
k=clear taken by



**LOG BOOK**  
Project **C96-032/041**  
Chlorpyrifos, ambient

log number	sample ID	date	time	comments	weather o=overcast pc=partly cloudy k=clear	taken by
45 B	ARB-8	6-10-96	1500			
		6-11-96	1100		K	L.J.J.
46 B	J-8	6-10-96	1545			
		6-11-96	1250			
47 B	S-8	6-10-96	1600			
		6-11-96	1315			
48 B	ARB-9	6-11-96	1100			
		6-12-96	1020			
49	J-9	6-11-96	1250			
		6-12-96	1105			
50	B-9	6-11-96	1315			
		6-12-96	1130			
51	K-9	6-11-96	1345			
		6-12-96	1210			
52	UC-9	6-11-96	1405			
		6-12-96	1245			
53	ARB-10	6-12-96	1020			
		6-13-96	0900			
54	ARB-10D	6-12-96	1020	DUPLICATE		
		6-13-96	0900			
55	J-10	6-12-96	1105			
		6-13-96	0940			
56	J-10D	6-12-96	1105	DUPLICATE		
		6-13-96	0940			
57	S-10	6-12-96	1130			
		6-13-96	1005			
58	S-10D	6-12-96	1130	DUPLICATE		
		6-13-96	1005			
59	K-10	6-12-96	1210			
		6-13-96	1045			
60	K-10D	6-12-96	1210	DUPLICATE		
		6-13-96	1045			
61	UC-10	6-12-96	1245			
		6-13-96	1120			
62	UC-10D	6-12-96	1245	DUPLICATE		
		6-13-96	1120			
63	ARB-11	6-13-96	0900			
		6-14-96	0835			
64	J-11	6-13-96	0940			
		6-14-96	0725			
65	S-11	6-13-96	1005			
		6-14-96	0705			
66	K-11	6-13-96	1045		✓	✓
		6-14-96	0745			

**LOG BOOK**  
**Project C96-032/041**  
 Chl orpyri fos, ambi ent

log number	sample ID	date	time	comments	weather o=overcast pc=partly cloudy k=clear	taken by
67	UC-11	6-13-96	1120			
		6-14-96	0805			
68	UC-11B	6-14-96	0805	BLANK		
		6-16-96	1215			
69	ARB12	6-17-96	1100		K	MTA
		6-16-96	1215			
70	QA1A	6-17-96	1100			
		6-16-96	1330			
71	K12	6-17-96	1200			
		6-16-96	1400			
72	S12	6-17-96	1245			
		6-16-96	1430			
73	J12	6-17-96	1315			
		6-17-96	1500			
74	UC12	6-17-96	1400			
		6-17-96	1100			
75	ARB13	6-18-96	1000			
		6-17-96	1100			
76	GA2A	6-18-96	1000			
		6-17-96	1200			
77	K13	6-18-96	1100			
		6-17-96	1245			
78	S13	6-18-96	1140			
		6-17-96	1310			
79	J13	6-18-96	1215			
		6-17-96	1400			
80	UC13	6-18-96	1300			
		6-18-96	1000			
81	ARB14	6-19-96	0900			
		6-18-96	1000			
82	ARB14D	6-19-96	0900	Duplicate		
		6-18-96	1000			
83	GA3A	6-19-96	0900			
		6-18-96	1100			
84	K14	6-19-96	0930			
		6-18-96	1140			
85	S14	6-19-96	1000			
		6-18-96	1215			
86	J14	6-19-96	1030			
		6-18-96	1300			
87	UC14	6-19-96	1100			
		6-19-96	0900			
88	ARB15	6-20-96	0800			

**LOG BOOK**  
 Project **C96-032/041**  
 Chlorpyrifos, ambient

log number	sample ID	date	time	comments	weather o-overcast pc=partly cloudy k-clear	taken by
89	QA4A	6-19-96	0900		K	NTA
90	QA5A	6-20-96	0900			
91	K15	6-19-96	0940			
92	K15D	6-20-96	0900	Duplicate		
93	S15	6-20-96	0940			
94	S15D	6-20-96	0940	Duplicate		
95	J15	6-19-96	1110			
96	J15D	6-20-96	1020	Duplicate		
97	UC15	6-19-96	1200			
98	UC15D	6-20-96	1145	Duplicate	V	✓
99	BLANK	6-20-96	1145		K	NTA
100	QA1B	6/20/96		QA TRIP		
101	QA2B	6/20/96		QA TRIP		
102	QA3B	6/20/96		QA TRIP		
103	QA4B	6/20/96		QA TRIP	V	✓
104	QA5B	6/20/96		QA TRIP		
105	ARB-16	6/24/96	1200		O	NTA
106	FAUCD-1	6/25/96	1100		O	
107	K14	6/24/96	1245		O	
108	S16	6/23/96	1315		O	
109	J16	6/23/96	1400		O	
110	UC16	6/24/96	1435		O	

**LOG BOOK**  
Project **C96-032/041**  
Chlorpyrifos, ambient

log number	sample ID	date	time	comments	weather o=overcast pc=partly cloudy k=clear	taken by
111	ARB17	6-25-96	1000		PC	NTA
112	FAUCD2	6-25-96	1100		PC	NTA
113	K17	6-25-96	1135		O	
114	S17	6-25-96	1205		O	
115	J17	6-25-96	1230		O	
116	UC17	6-25-96	1345		O	
117	ARB18	6-26-96	1000		PC	
118	ARB18	6-27-96	0910	Duplicate	PC	
119	FAUCD3	6-26-96	1000		PC	
120	K18	6-27-96	0950		PC	
121	K18D	6-26-96	1040	Duplicate	PC	
122	S18	6-27-96	1110		PC	
123	S18D	6-26-96	1110	Duplicate	PC	
124	J18	6-26-96	1130		PC	
125	J18D	6-27-96	1100	Duplicate	PC	
126	UC18	6-26-96	1235		PC	
127	UC18D	6-27-96	1135	Duplicate	PC	
128	ARB19	6-27-96	0910		K	
129	FAUCD4	6-28-96	1115		K	
130	K19	6-27-96	0950		K	
131	S19	6-27-96	1030		K	
132	J19	6-27-96	1100		K	

# LOG BOOK

Project

C96-032/041

Chlorpyrifos, ambient

weather  
o=overcast  
pc=partly cloudy  
k=clear taken by

E -  
S -  
W -  
A -

122  
samples 3+5 at East side

LOG BOOK  
Project C96-032A/040  
Chlorpyrifos, application

log number	sample ID	date	time	comments	weather o=overcast pc=partly cloudy k=clear	taken by
1	E-1	6/3/96 6/4/96	2120 0555	background	K K	HEH
2	E-1A	6/3/96 6/4/96		VOID	K K	1
3	S-1	6/3/96 6/4/96	2110 0540	background	K K	
4	W-1	6/3/96 6/4/96		VOID	K K	
5	N-1	6/3/96 6/4/96	2125 0605	background	K K	
6	S-2	6/4/96 6/4/96	0550 1130	start of application 0630	K	
7	E-2	6/4/96	0555 1135		K	
8	E-2D	6/4/96	0555 1135		K	
9	N-2	6/4/96 6/4	0600 1125		K	
10	S-3	6/4/96 6/4	1130 1315		K	
11	E-3	6/4/96 6/4	1135 1315	5:13.5	K	
12	E-3D	6/4/96 6/4	1135 1315		K	
13	N-3	6/4/96 6/4	1125 1310		K	
14	N-4	6/4 6/4	1310 1730		K	
15	S-4	6/4 6/4	1315 1735	5:30pm	K	
16	E-4	6/4 6/4	1320 1740		K	
17	E-4D	6/4 6/4	1320 1740		K	
18	N-5	6/4 6/5	1730 0400		K	
19	S-5	6/4 6/5	1735 0405		K	
20	E-5	6/4 6/5	1740 0410		K	
21	E-5D	6/4 6/5	1740 0410		K	
22	N-6	6/5 6/5	0400 1235	start of application 0430 * flow dropped to 13.5	K K	1

No Sample  
Taken →

stolen →

5:40

**LOG BOOK**  
 Project **C96-032A/040**  
 Chlorpyrifos, application

log number	sample ID	date	time	comments	weather o=overcast pc=partly cloudy k=clear	taken by
23	S-6	6/5	0405		K	
		6/5	1240		K	KEM
24	E-6	6/5	0410			
		6/5	1245			
25	E-6D	6/5	0410			
		6/5	1245			
26	N-7	6/5	1235			
		6/6	0605			
27	S-7	6/5	1240			
		6/6	0610			
28	E-7	6/5	1245			
		6/6	0615			
29	E-7D	6/5	1245			
		6/6	0615			
30	APPB-1	6/5	1245	Application Blank	↓	KEM
		6/6	—			
31	N-8	6/6	0605		K	DEP
		6/7	0605			
32	S-8	6/6	0610			
		6/7	0610			
33	E-8	6/6	0615			
		6/7	0615			
34	E-8D	6/6	0615			
		6/7	0615			
35	N-9					
36	S-9					
37	E-9					
38	E-9D					
39						
40						
41						
42						
43						
44						

APPENDIX VII  
METEOROLOGICAL DATA



Date June/1996	Time	Wind Speed (mph)	Wind Direction (01360 = mag north)	Wind Direction (compass)	Temperature ICI	Relative Humidity
3	1606	3.64	265.5	W	45.69	26.06
3	1621	9.41	266.5	W	45.19	30.49
3	1636	9.64	260.7	W	41.48	33.69
3	1651	3.78	230.7	SW	41.24	34.32
3	1706	7.67	292.5	NW	41.29	34.28
3	1721	7.66	317.8	NW	41.10	34.23
3	1736	8.03	262.1		40.85	34.86
3	1751	7.47	275.1	W	40.65	35.46
3	1806	7.22	275.4	W	40.13	36.17
3	1821	7.24	261.11		39.361	37.98
3	1836	6.34	276.91	W	38.34	39.88
3	1851	5.33	270.9	W	37.82	41.15
3	1906	5.1	293.2	NW	36.72	43.09
3	1921	5	276.8	W	35.69	45.1
3	1951	2.071	286.41	NW	34.08	48.2
						50.86
3	2006	4.391	304.31	NW	31.391	53.98
3	2021	4.34	291.6	W	29.79	57.81
3	2036	3.77	275.6	W	29.34	59.2
3	2051	4.13	279.3	W	29.72	58.01
3	2106	4.48	250.9	W	29.79	58.09
3	2121	5.01	252.9		29.16	59.44
3	2136	4.31	266.3	W	28.83	60.54
3	2151	1.81	146.3	SE	27.13	63.64
3	2206	1.25	132.6	SE	27.08	63.87
3	2221	2.27	157.1	SE	25.43	68.07
3	2236	1.74	104.3	E	24.6	69.62
3	2251	1.63	118.3	SE	23.71	72.5
3	2306	3.511	132.91	SE	23.131	73.9
3	2321	2.61	130.41	SE	24.131	71
3	2336	3.38	169.8	S	24.09	71.4
3	2351	2.86	140.2	SE	22.75	74.6
4	6	2.82	237.5	SW	22.65	75.4
4	21	1.1	230.4	SW	22.86	74.7
4	36	0.9	114.1	SE	21.82	77.9
4	51	2.83	115.5	SE	22.01	77.1
4	106	0.89	131.5	SE	21.94	77.4
4	121	2.07	157	SE	21.41	78.7
4	136	1.57	53.26	NE	21.1	80
4	151	1.51	55.63	NE	20.51	81.9
4	206	0.68	151.8	SE	20	84.2
4	221	1.92	142.8	SE	19.67	85.2
4	236	1.05	70.1	E	19.381	86.4
4	251	0.76	72.5	E	19.341	86.5
4	306	2.09	28	NE	19.02	87.8
4	321	1.48	205.6	SW	19.01	87.8
4	336	4.66	211.5	SW	19.25	86.5

Date June/1 996	Time	Wind Speed (mph)	Wind Direction (0/360 = mag north)	Wind Direction (compass)	Temperature (C)	Relative Humidity
4	351	0.46	194	S	19.2	87.2
4	406	1.39	84.3	E	18.67	89.1
4	421	1.32	90.5	E	18.88	88.5
4	436	0.84	172.5	S	18.62	89.2
4	451	1.77	45.56	NE	18.3	91.1
4	506	3.79	9.5	N	18.29	91.1
4	521	2.14	49.51	NE	18.29	91.8
4	536	1.93	99.5	E	18	92.4
4	551	1.76	53.23	NE	17.96	93.1
4	606	1.07	84	E	18.22	91.8
4	621	2.11	73.5	E	18.74	89.3
4	636	1.48	110.6	E	19.77	85.1
4	651	2.05	81.1	E	21.07	80.3
4	706	1.76	105.6	E	22.37	75.9
4	721	1.7	104.6	E	23.41	72.7
4	736	3.43	82.1	E	25.03	68.65
4	751	3.42	84.71	E	25.61	66.92
4	821	2.71	108.4	E	30.13	66.11
						63
4	836	2.95	86.4	E	28.67	59.77
4	851	3.69	110.81	E	29.74	57.78
4	906	3.42	122.8	SE	30.68	55.55
4	921	4.48	89.1	E	31.59	53.82
4	936	12.77	145.3	SE	32.24	52.46
4	951	9.63	150.2	SE	32.04	53.05
4	1006	7.98	120.9	SE	32.37	52.37
4	1021	11.4	152.5	SE	32.59	51.65
4	1036	8.13	193.4	S	33.08	50.96
4	1051	6.48	211.3	SW	32.89	50.91
4	1106	9.77	173.1	S	33.73	49.6
4	1121	8.41	202.9	S W	34.32	48.29
4	1136	7.86	203.3	S W	34.64	47.61
4	1151	7.32	223.8	S W	35.14	46.93
4	1206	8.62	202.91	-SW	35.55	45.61
4	1221	7.89	164.7	S	35.61	45.58
4	1236	6.19	159.81	S	36.19	44.92
4	1251	8.7	156.51	SE	37.03	43.51
4	1306	6.77	182.71	S	37.87	41.72
4	1321	4.33	241.8	S W	38.56	40.42
4	1336	5.69	223.2	S W	39.9	37.85
4	1351	5.65	172.8	S	39.61	38.51
4	1406	2.84	8.78	N	40.62	36.76
4	1421	3.45	196	S	41.26	35.59
4	1436	5.37	284	WI	41.62	34.87
4	1451	7.26	330.2	N W	41.68	34.91
4	1506	7.36	285.7	W	42.43	33.46
4	1521	8.69	291.1	W	41.44	34.86

Date June/1996	Time	Wind Speed (mph)	Wind Direction (0/360 = mag north)	Wind Direction (compass)	Temperature (C)	Relative Humidity
4	1536	6.85	313.1	NW	41.84	34.19
4	1551	10.22	290.71	W	41.17	35.41
4	1606	9.79	290.31	W	41.34	35.41
4	1621	8.6	319	NW	41.41	34.81
4	1636	7.39	279.51	W	41.11	35.37
4	1651	9.46	290.3	W	40.04	36
4	1706	8.05	293.51	NW	40.85	35.98
4	1721	7.47	281.6	W	40.9	35.38
4	1736	9.33	301.31	NW	40.27	35.96
4	1751	8.17	302.6	NW	40.65	35.97
4	1806	8.97	308.6	NW	40.22	37.14
4	1821	8.33	270.6	W	39.85	37.9
4	1836	6.17	296.9	NW	39.27	39.08
4	1851	5.53	267	W	38.15	41.1
4	1906	5.54	303	NW	37.44	42.37
4	1921	4.55	303.3	NW	36.36	44.31
4	1936	4.35	326.8	NW	34.67	47.7
4	1951	3.6	292.8	NW	32.92	51.35
4	2006	3.35	295.2	NW	30.89	55.84
4	2021	3.2	327	NW	29.38	59.15
4	2036	0.74	100.2	E	27.61	62.57
4	2106	1.94	20.38	NE	26.43	65.59
4	2121	4.96	294.1	NW	28.59	61.18
4	2136	6.63	312.5	NW	28.77	60.45
4	2151	6.75	283.5	W	28.68	60.42
4	2206	5.56	290.5	W	28.07	61.66
4	2221	2.94	328.3	NW	27.43	63.24
4	2236	2.93	263.3	W	26.43	65.5
4	2251	5.95	290.51	W	25.59	67.57
4	2306	3.74	81	E	25.52	68.14
4	2321	0.78	242.5	SW	24.37	70.7
4	2336	3.15	238.8	SW	23.84	72
4	2351	2.25	101.6	E	24.12	71.5
5	24	2.86	132.14	SW	22.75	77.1
5	36	2.1	60.65	NE	20.98	80.5
5	51	0.49	214.7	SW	20.68	81.2
5	106	2.87	223.5	SW	21.16	79.9
5	121	1.72	143.6	SE	20.32	83
5	136	2.34	137.1	SE	19.74	85.1
5	151	2.64	189.5	S	19.67	85.2
5	206	2.28	128.4	SE	19.08	87.6
5	221	1.27	100.6	E	18.57	90.3
5	236	1.9	98.5	E	18.24	91.7
5	251	1.76	129.9	SE	18.21	92.3
5	306	2.69	141.8	SE	18.17	91.7

Date June/1996	Time	Wind Speed (mph)	Wind Direction (0/360 = mag north)	Wind Direction (compass)	Temperature (C)	Relative Humidity
5	321	2.71	151.1	SE	18.12	92.3
5	336	2.8	100.1	E	17.84	93.3
5	351	2.61	110.7	E	17.83	93.6
5	406	2.47	123.8	SE	18.03	93
5	421	3.35	72.1	E	17.77	94.3
5	436	1.47	93.5	E	17.49	95
5	451	1.28	96.2	E	17.44	95.6
5	506	1.7	56.94	NE	17.18	96.9
5	521	1.94	67.42	NE	17.14	97.6
5	536	4.2	90.8	E	17.38	96.9
5	551	2.37	95.2	E	17.63	95.1
5	606	2.57	181.91	S	17.61	95.1
5	621	0	5.11	N	17.82	93.2
5	636	1.51	83	E	18.35	90.7
5	651	2.92	142.4	SE	19.51	85.7
5	706	3.88	101.3	E	20.72	81.1
5	721	4.74	110	E	21.78	78
5	736	3.03	121.4	SE	22.55	75.6
5	751	4.91	142.2	SE	23.66	72.6
5	806	7.44	135.3	SE	24.41	70.8
5	821	4.11	176.21	S	25.08	68.81
5	836	6.45	151.7	SE	26.27	65.55
5	851	7.85	138.9	SE	26.85	64.23
5	906	7.31	135.5	SE	27.18	63.54
5	921	5.41	221.7	SW	27.76	62.23
5	936	6.46	154.8	SE	28.53	60.71
5	951	6.71	196.1	S	29	59.54
5	1006	5.9	169.9	S	29.89	57.55
5	1021	4.93	183.7	S	30.23	56.86
5	1036	5.07	184.2	S	30.58	56.18
5	1051	7.31	159.8	S	30.88	55.49
5	1106	8.76	153.5	SE	31.47	54.23
5	1121	6.38	199.4	S	32.09	52.84
5	1136	3.14	163.8	S	32.95	50.87
5	1151	8.48	217.4	SW	33.79	49.61
5	1206	5.85	162.8	S	33.86	49.51
5	1221	6.24	220	SW	34.96	46.98
5	1236	1.02	97.2	E	35.03	46.88
5	1251	5.26	222.1	SW	36.12	45.18
5	1306	4.54	212.9	sw	36.72	43.62
5	1321	5.58	214.6	SW	37.29	42.95
5	1336	5.28	203.91	SW	37	41.68
5	1351	4.3	209	S W	37.96	41.68
5	1406	6.38	240.3	S W	39.05	39.71
5	1421	5.25	278.8	W	39.92	37.76
5	1451	6.678	317.59	NW	39.74	38.42

Date June/1996	Time	Wind Speed (mph)	Wind Direction (0/360 = mag north)	Wind Direction (compass)	Temperature (C)	Relative Humidity
5	1506	6.27	277.6	W	39.87	37.91
5	1521	4.27	214	SW	40.33	37.18
5	1536	5.3	301.5	NW	40.42	37.29
5	1551	4.92	328.1	NW	40.78	36.57
5	1606	5.88	282	W	40.58	36.6
5	1621	8.33	296.8	NW	40.93	35.96
5	1636	8.09	277.2	W	41.16	35.36
5	1651	6.65	266.1	W	40.53	36.67
5	1706	8.03	265.7	W	40.71	36.61
5	1721	9.24	272	W	40.88	35.93
5	1736	6.05	247	SW	39.86	37.85
5	1751	5.7	266.9	W	39.68	38.45
5	1806	8.49	278.2	W	39.16	39.11
5	1821	7.1	282.8	W	38.59	40.4
5	1836	6.78	271.1	W	38.12	41.01
5	1851	4.62	264.9	W	37.5	42.32
5	1906	3.68	289.3	W	36.87	43.58
5	1921	2.57	276.2	W	35.88	45.51
5	1936	1.81	303.1	NW	34.79	47.88
5	1951	1.56	300	NW	33.17	50.94
5	2006	1.83	326.3	NW	31.05	54.98
5	2021	2.06	41.16	NE	29.47	58.63
5	2036	2.73	331.2	NW	28.98	59.95
5	2051	2.91	298.41	NW	29.36	59.37
5	2106	4.08	278	W	28.71	60.14
5	2121	3.391	267.51	W	27.96	62.07
5	2136	2.12	170.2	S	26.34	65.93
5	2151	2.571	112.11	E	24.58	69.87
5	2206	2.69	127.6	SE	24.43	70.8
5	2221	3.46	125.3	SE	24.3	71.3
5	2236	2.95	132.4	SE	23.2	73.8
5	2251	1.97	137.2	SE	23.13	74
5	2306	2.14	123	SE	23.1	74.6
5	2321	1.71	135.1	SE	22.54	75.9
5	2336	3.21	102.71	E	21.96	77.2
5	2351	2.02	104.6	E	22.15	77
6	6	2.471	157.61	S	21.89	78.5
6	21	1.74	129.3	SE	21.8	78.6
6	36	1.561	137.11	SE	21.33	79.9
6	51	2.82	145.1	SE	21.18	79.9
6	106	1.75	112.8	SE	21.14	80.5
6	1211	2.48	133.9	SE	21.09	80.6
6	136	2.5	141.5	SE	20.8	81.3
6	151	2.61	83	E	20.51	82.1
6	206	2.07	114.1	SE	20.56	81.9
6	2211	2.07	102.21	E	20.371	83.2
6	236	1.49	84	E	19.93	84.5

Date June/ 1996	Time	Wind Speed (mph)	Wind Direction (0/360 = mag north)	Wind Direction (compass)	Temperature (C)	Relative Humidity
6	251	2.05	186.5	S	19.62	85.8
6	306	1.381	169.31	S	20.12	84
6	321	2.241	119.91	SE	20.381	82.7
6	336	1.91	78.91	E	19.93	84.6
6	351	1.69	257.2	W	19.01	87.8
6	406	1.6	174.7	S	19.06	87.8
6	421	3.16	150	SE	18.95	88.5
6	436	1.02	55.57	NE	19.72	85.8
6	451	1.921	79.91	E	18.89	89.2
6	506	4.341	123.51	SE	18.691	89.2
6	521	1.91	73.6	E	18.88	89.2
6	536	1.03	72.8	E	18.36	90.6
6	551	3.08	84.7	E	18.61	89.8
6	606	1.91	142	SE	18.82	89.2
6	621	2.381	160.11	S	19.021	88.5
6	636	3.481	118.51	SE	20.07	84.1
6	6511	4.581	139.41	SE	20.88	81
6	706	4.79	142.1	SE	21.91	77.9
6	721	4.081	101.61	E	23.02	74.6
6	736	6.261	141.71	SE	24.341	71.3
6	751	3.491	91.2	E	25.19	68.14
6	806	3.99	85.7	E	26.01	66.8
6	821	4.22	128.1	SE	26.85	64.65
6	836	3.67	184	S	27.86	62.24
6	851	4.29	168.3	S	28.86	59.86
6	906	3.64	161.1	S	29.45	58.89
6	921	2.28	271.1	W	30.29	56.55
6	936	2.94	198.4	S	30.94	55.62
6	951	4.97	214.7	SW	31.52	54.32
6	1006	5.961	183.2	S	31.61	53.66
6	1021	7.3	184.4	S	32.24	52.91
6	1036	6.29	180.2	S	32.64	52.03
6	1051	8.61	149.2	SE	33.39	50.91
6	1106	4.04	149.2	SE	33.22	50.87
6	1121	..	119.9	SE	34.07	48.94
6	1136	3.71	133.81	SE	34.67	47.62
6	1151	6.17	162.2	S	35.27	46.89
6	1206	3.44	127.5	SE	35.87	45.57
6	1221	2.39	158.9	S	36.97	43.13
6	1236	7.21	154.1	SE	37.03	43.58
6	1251	4.94	130.7	SE	36.84	43.84
6	1306	4.75	205.5	S W	37.98	41.59
6	1321	4.93	258	W	38.78	40.28
6	1336	2.77	247.4	S W	39.36	38.97
6	1351	4.94	295.5	N W	39.94	37.66
6	1406	2.91	266.9	W	40.78	36.35
6	1421	3.88	275.9	W	41.13	35.5

Date (C) /1996	Time	Wind Speed (mph)	Wind Direction (0/360 = mag   th)	Wind Direction (compass)	Temperature	Relative Humidity
40	6 1436	6.03	3971.6	W	40.45	36.89
6	1451	5.66	293.71	NW	40.451	36.851
6	1506	6.23	277.7	W	40.78	36.17
6	1521	5.72	276.5	W	41.61	34.62
6	1536	7.51	216.81	SW	41.181	34.68
6	1551	6.03	247.3	SW	40.58	36.3
6	1606	8.74	256.1	W	40.9	36.11
6	1621	6.25	291	W	40.97	35.46
6	1636	7.191	309.71	NW	40.461	36.09
6	1651	9.44	296.4	NW	40.22	36.8
6	1706	7.72	261.51	W	40	37.37
6	1721	7.59	266.2	W	40	37.31
6	1736	7.331	260.91	W	39.73	37.98
6	1751	6.24	266.8	W	39.43	38.65
6	18061	4.931	296.31	NW	39.171	39.29
6	18211	7.041	253.21	W	38.471	40.17
6	1836	6.07	280.9	W	37.91	41.23
6	1851	6.21	278.4	W	37.26	42.48
6	1906	4.6	254.4	W	36.39	44.35
6	1921	3.08	277.8	W	35.35	46.29
6	1936	1.56	266.1	W	34.28	48.23
6	1951	1.37	7.1	N	33.12	50.81
6	2006	1.09	92.2	E	31.56	54.02
6	2021	1.22	84.5	E	30.14	57.09
6	2036	1.32	139.2	SE	29.75	58
6	2051	2.09	112.8	SE	28.6	60.59
6	2106	1.46	125.1	SE	27.92	62.55
6	2121	2.25	125.4	SE	27.37	63.31
6	2136	2.11	121.8	SE	26.77	64.69
6	2151	1.67	128.6	SE	25.88	66.62
6	2206	2.66	96.9	SE	25.79	66.8
						68.62
6	22361	2.061	111.81	E	24.88	69.32
6	22511	1.421	134.9	SE	24.56	70.2
6	23211	2.9511	159.71	SE	24.176	71.2
						71.3
6	23361	1.891	41.07	NE	23.65	72.6
7	2356	3.881	183.2	E	23.03	74.5
						73.3
7	21	1.35	207.6	SW	22.99	74.6
7	36	0.271	255.81	W	22.671	75.3
7	51	0.97	69.2	E	22.15	77.2
7	106	4.43	46.25	NE	22.341	76.6
7	121	2.02	23.3	NE	22.04	77.3
7	136	1.491	268.91	W	21.471	79.3
7	151	1.1641	369.6	E	21.22	79.9
				NE	21.91	78.3

Date		Wind Speed	Wind Direction (0/360 =	Wind Direction	Temperature	Relative Humidity
June/1996	Time	(mph)	mag north)	(compass)	(C)	
7	221	2.141	123.11	SE	22.18	76.8
7	236	2.68	115.1	SE	21.79	78.6
7	251	2.321	120.91	SE	21.23	80
7	301			E	20.77	81.3
7	326	3.70	101.6 97.3	E	20.5	82.6
7	336	4.7	119.9	SE	20.71	81.3
7	351	3.25	138.1	SE	20.71	81.9
7	406	3.52	137.7	SE	20.96	80.7
7	421	4.81	118.5	SE	21.22	80.1
7	436	1.11	86.4	E	20.44	82.3
7	451	1.52	67.45	NE	19.6	85.8
7	506	2.69	89.1	E	19.6	85.8
7	521	5.41	86.4	E	20.12	84.6
7	536	4.27	91.9	E	20.26	83.3
7	551	0.46	103.6	E	20.05	84.2
7	606	1.87	72.2	E	19.79	83.3
7	621	1.49	102.6	E	20.05	84.4
7	636	1.21	128.31	SE	21.06	80.8
7	651	1.41	125.2	SE	22.12	77
7	706	2.35	104.91	E	23.16	74.4
7	721	2.261	118.9	SE	24.19	71.3
7	736	4.281	112.8	SE	25.29	68.64
7	751	4.52	112.2	E	25.98	66.77
		4.471	157.8	S	26.66	64.81
7	836	5.541	109.59	SE	27.5	62.86
					28.48	60.9
7	906	5.591	119.6	SE	29.461	58.93
						56.32
7	921	5.251	126.71	SE	30.50	54.19
7	936	5.421	140.91	SE	32.86	51.47
7	9511	6.331	141.1	SE	32.95	51.69
7	10061	8.191	114.5	SE	33.02	51.03
7	1021	3.54	120.2	SE	33.37	50.42
7	1036	6.13	193.7	S	34.25	48.97
7	1051	6.79	205.4	SW	34.29	48.92
7	1106	7.03	183.7	S	34.12	48.87
7	1121	4.13	160.9	S	34.191	48.133